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APRIL 1963

PROJECT NEOS

A GENERAL STUDY OF PROCESSES FOR THE REALIZATION OF DESIGN CONFIGURATIONS IN MATERIALS

Paul Rosenthal

CORNELL AERONAUTICAL LABORATORY

CONTRACT: AF 33(600)-42921

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FOURTH INTERIM TECHNICAL REPORT

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The studies of manufacturing process elements that were the subject of earlier interim reports are now serving as inputs to systematic process synthesis. Highlights of this report are concepts for two new process categories that exploit phenomena better known for their destructive effects: cavitation and spontaneous oxidation.

MANUFACTURING TECHNOLOGY LABORATORY
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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of earlier interim reports are now serving as inputs to systematic process
synthesis. Highlights of this report are concepts for two new process cate-
gories that exploit phenomena better known for their destructive effects:
cavitation and spontaneous oxidation.

General guidelines for process synthesis are developed based on the
material properties, topological characteristics of the processes, the
energy transformation involved and the environmental conditions essential
to the energy transfer. In later sections of the report, these characteristic
features of material removal, material joining, and material displacement
processes are developed.

Two general approaches to improving material removal processes
are cited: The first is concerned with reducing surface energy by environ-
mental means, the second with modification of the geometry of the failure
mechanism, so as to reduce the energy required. Material removal
processes synthesis includes microscopic and macroscopic aspects of
relaxation and resonance in materials, cavitation, and chemical removal.

The approach to improving the joining processes is directed at the
control of surface preparation and the removal of the energy released due
to reduction of total surface area. Examples presented include the category
of diffusion bonding processes, means for achieving shape control in vapor
deposition and a process category in which a liquid medium is temporarily
interposed between the mating surfaces.

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Improved material displacement processes are shown to result - from the energy point of view - from reduction in the number and distances of discrete particle displacements necessary for the process. Synthesis is discussed on macroscopic and microscopic levels. As a hypothetical example a displacement process involving combinations of magnetic, thermal and electrical energy is outlined.

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FOREWORD

This interim report covers the work performed under Contract AF 33(600)-42921 from 3 November 1962 to 3 April 1963. It is published for technical information only and does not necessarily represent the recommendations, conclusions, or approval of the Air Force.

The contract with the Cornell Aeronautical Laboratory, Inc., Buffalo 21, New York, was initiated under ASD Project NR 7-867, "A General Study of Processes for the Realization of Design Configuration in Materials." It is administered under the direction of Mr. W. M. Webster, ASRCTF, Manufacturing Technology Laboratory, Aeronautical Systems Division, Air Force Systems Command, United States Air Force, Wright-Patterson Air Force Base, Ohio.
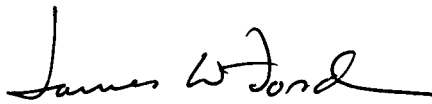
Mr. Paul Rosenthal, Head of the Mechanical Engineering Section of the Laboratory's Applied Physics Department, is the project engineer. Others who cooperated in the research and in the preparation of the report were Mr. H. T. McAdams, Principal Physicist, Mr. W. R. Brown, Dr. N. S. Eiss, Mr. J. R. Graham, Mr. P. J. Joseph, Mr. P. W. Langhoff and Mr. J. D. Myers of the Cornell Aeronautical Laboratory. The following persons participated as consultants to the project: Professor N. H. Cook of MIT, Professors H. H. Johnson and M. S. Burton of Cornell University, Mr. W. Pentland, Therm Inc., and Professor B. F. von Turkovich, University of Illinois.

The primary objective of the Air Force Manufacturing Methods Program is to increase producibility and improve the quality and efficiency of fabrication of aircraft, missiles, and components thereof. This report is being disseminated so that those interested in the development of new manufacturing processes, the goal of the program, may participate in its progress from the outset.

Your comments are solicited on the potential use of the information contained herein as applied to your present or future production programs. Suggestions concerning your requirements for manufacturing methods development will be appreciated.

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PUBLICATION REVIEW

APPROVED BY:

James W. Ford, Head
Applied Physics Department

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1. INTRODUCTION

Under Contract No. AF 33(600)-42921 for the Air Force Aeronautical Systems Division (ASD Project NR 7-867), Cornell Aeronautical Laboratory, Inc., is conducting Project NEOS, a systematic search to identify for further development new manufacturing processes.

Many of the unconventional approaches to manufacturing methods have arisen on an ad hoc basis, i.e., they have been addressed to producibility problems associated with specific materials in specific aerospace systems. As a result, there is an undesirable time lag in the development of manufacturing methods applicable to new materials. Project NEOS is aimed at eliminating this time lag by a systematic search for principles capable of leading to order-of-magnitude improvements in manufacturing processes.

To admit unconventional procedures, the definition of the term "manufacturing process" has been broadened to include the entire train of events from the time a material comes into being as a distinct substance until that substance is made to assume a desired configuration. Consequently, the project has as its objective an investigation of engineering materials at atomic, molecular, or other suitable levels and a determination of the kinds and magnitudes of energies required to produce useful configurations with acceptable properties and tolerances.

Earlier in the program, our studies were concentrated on these elements of the manufacturing process: (1) the characteristics of the energy employed in transforming the material into the desired configuration; (2) the material from which the configuration is to be realized; (3) the environment required for the transformation to be effective; and (4) the means by which energy is applied to the material under adequate control for the process.

This report reflects our increasing concentration on process synthesis, to which the process element studies previously performed and still under way are inputs. Following the development of general guidelines for process synthesis (in Section 2), the approach to the synthesis of material removal, addition, and displacement processes is discussed in Sections 3, 4 and 5.

The program for the next 6-month period is outlined in Section 6. The Appendices contain detailed accounts of studies on Chemical Material Removal Processes (A), Shape Control in Vapor Deposition (B), Cavitation (C), and Electric Effects in Ionic Crystals (D).

2. GUIDELINES FOR PROCESS SYNTHESIS

A manufacturing process consists of a sequence of changes in material dimensions d and material properties p, as shown in Figure 1.

In this figure d is a vector denoting dimensions of interest and p is a vector denoting material properties. Though a practical process involves changes in both d and p as a function of time, t, it is conceivable that some processes might be "degenerate," in the sense that the path from A to B lies entirely in either the (d, t)-plane or the (p, t)-plane. In this sense, a process could involve dimensional changes only or material property changes only.

Dimensional changes in a workpiece can be effected, in general, by the processes of material addition, material deformation, or material removal. In this report, each category will be examined from the standpoint of its basic characteristics and the means whereby improvements or innovations can be achieved.

Any process can be considered in terms of the means by which controlled configurational changes can be induced in materials. Elements affecting the process, therefore, are the material undergoing configurational change, the topology of these changes, the energy transformations involved, and the environmental conditions essential to energy transfer.

In view of the fact that dimensional changes are often accompanied by changes in material properties during a process, it is natural to consider means whereby material properties can be modified to facilitate the desired dimensional changes. Examples of material modification for such purposes are hot forming and the use of free-machining additives. Material properties retained by the finished product must, of course, be consistent with use requirements, and it is this fact which limits an indiscriminate use of material modification for manufacturing purposes.

Within the framework of admissible material modifications, a range of processing possibilities exists. In most instances there may be many conceivable routes by which one may proceed from the initial to the final state in Figure 1. One of the aims of manufacturing technology is to find a route

DIMENSIONS
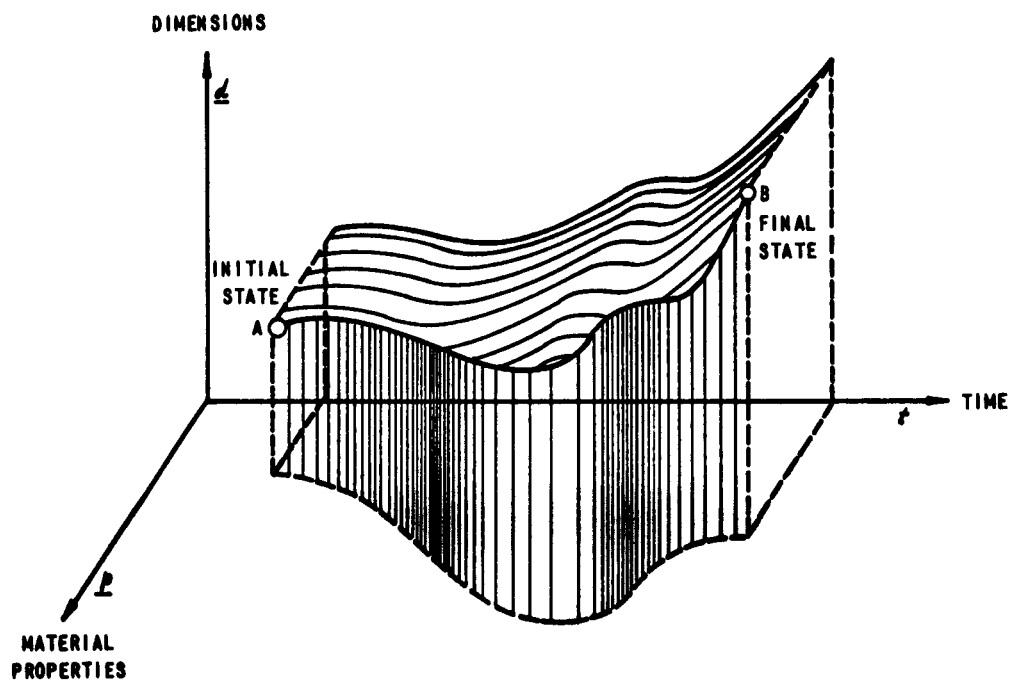
Figure I   ABSTRACT CONCEPT OF THE MANUFACTURING PROCESS

which is optimum in some meaningful sense. For example, in some cases it may be possible to produce a given configuration by either drawing or swaging, but the material involved may tolerate greater deformation before fracture in the one case than in the other.

Process topology denotes the mathematical description of the sequence of configurational changes involved in a manufacturing process. Significant improvements can often be achieved by an unconventional approach to manufacturing topology. For example, as will be indicated in a later section, many chip-forming cutting processes are inefficient, in the topological sense, because they involve a considerable amount of material deformation having little direct relation to the desired change in configuration. In general, we will seek novel topological approaches to the generation of a desired end configuration. In particular, there is evidence to indicate that in deformation processes it is advantageous to avoid tensile stresses wherever possible in order to discourage the formation of voids which might eventually lead to fracture. For such reasons, the importance of process topology is not to be overlooked, and a broad look at the topological features of processes in general is justified. In many instances, for example, it may be necessary to consider material addition, deformation, and removal as only parts of an over-all process requirement. Consequently, though these three categories provide a convenient systematization for study, they are not to be regarded in isolation from each other.

Material behavior in any of the three major categories of processes is often strongly influenced by the form of energy used to effect the desired configurational changes. For example, many of the newer aerospace materials have low tolerance for mechanical energy and hence must be shaped by other means, e.g., by chemical or electrical energy.

Mechanical, chemical, thermal, electrical and magnetic energy are forms of energy having identifiable effects on materials. These effects can be interrelated in a variety of ways with varying degrees of emphasis on mechanical, chemical, thermal, electrical, and magnetic aspects. If these five forms of energy are combined in all possible ways, one obtains

$$\sum_{i=1}^{5} C_i^5 = 2^5 - 1 = 31$$

possibilities, each of which might represent a <u>class</u> of manufacturing processes. The number of possible combinations of the forms of energy taken 1, 2, 3, 4, and 5 at a time respectively are given by the binomial coefficients 5, 10, 10, 5, 1. These enumerated possibilities form a partially-ordered system, as shown in Figure 2. By a partially-ordered system is meant one in which certain inclusion relations exist among its elements. In the figure, each class includes as a sub-class all those categories appearing below it to which it is joined by a line segment. For example, the class of all mechanical processes can be considered as containing, as sub-classes, all processes involving mechanical energy and any other combination of energy forms. Following various paths through the lattice suggests how the gamut of all possible combinations might be systematically explored. Furthermore, the number of combinations is a manageable one and admits critical examination of every point in the lattice without a prohibitive amount of time.

It is to be expected that in most instances, even when a single form of energy seems to predominate, certain contributing factors will be present in the form of general environmental factors essential to the success of the process even though they may not contribute any large amount of energy to the process. Examples of the importance of environmental factors are found in the need for a high vacuum for vapor deposition processes and the advantages achieved by lubricants in cutting and forming processes.

In the following three sections initial efforts at postulating new processes for material removal, material joining and material displacement are described.
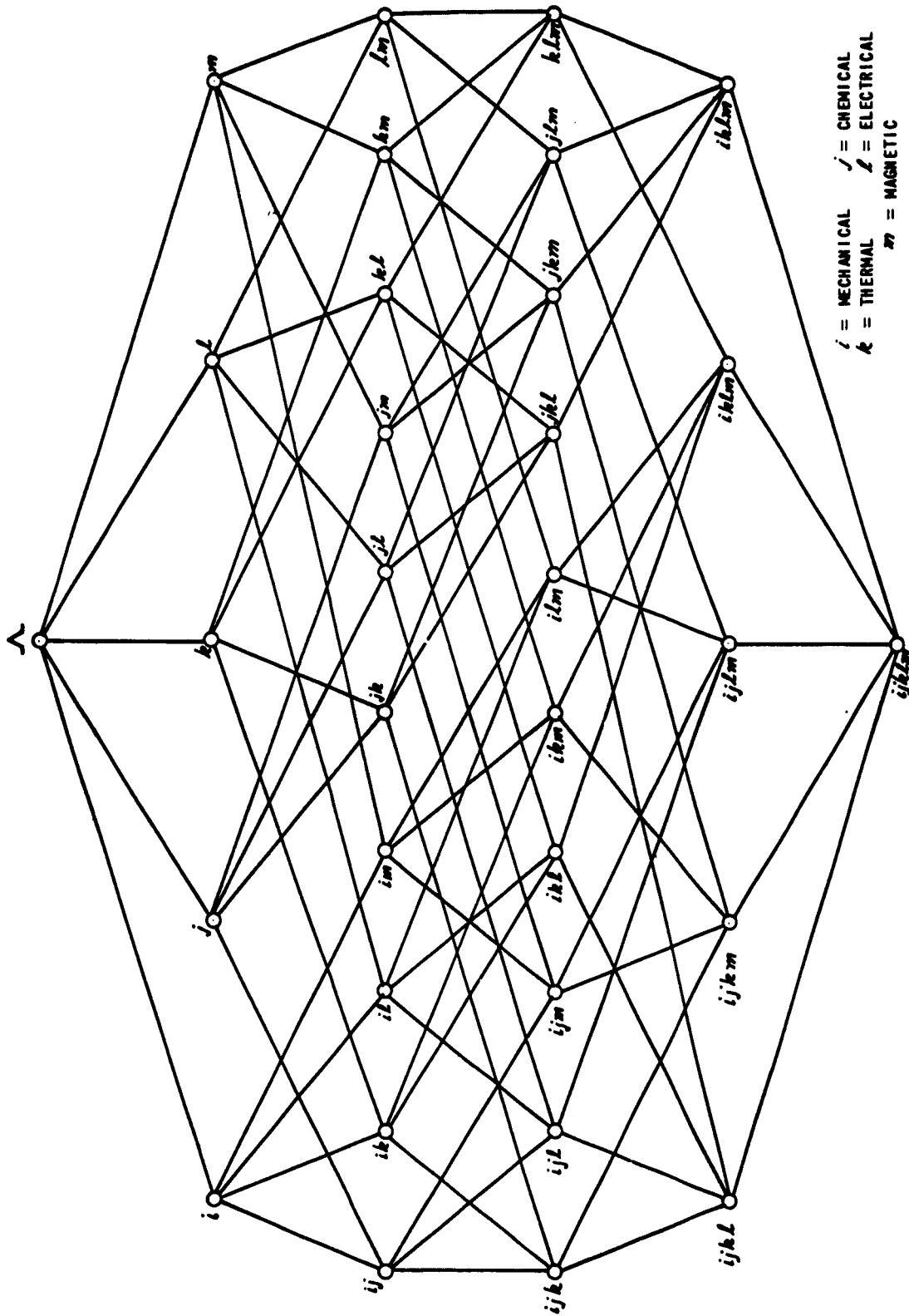
Figure 2 ENERGY SYSTEMS AND SUBSYSTEMS

i = MECHANICAL j = CHEMICAL
k = THERMAL l = ELECTRICAL
m = MAGNETIC

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3. MATERIAL REMOVAL PROCESSES

3.1 General Considerations

Ideally, a part or configuration is distinguished from its surrounding environment by a surface or interface. It is this discontinuity which defines the configuration. Consequently, a material-removal process can be considered, in the ideal sense, as a means for generating new surfaces.

Consider, for example, Figure 3.
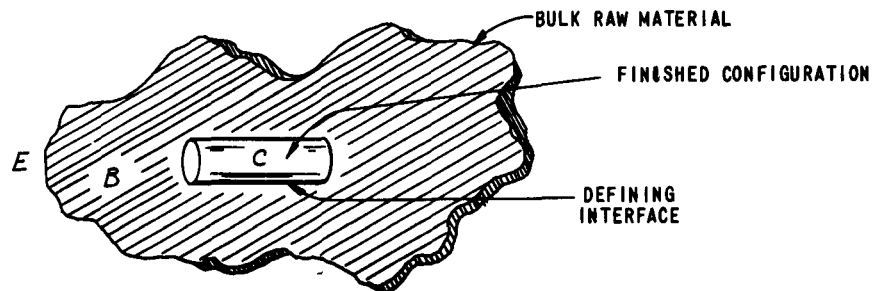
Figure 3 TOPOLOGY OF A MATERIAL REMOVAL
PROCESS

The object is to remove, in the most expeditious manner, material B so as to leave configuration C. Though many approaches to the problem are conceivable, these approaches all fall within an envelope bounded by two extremes. In the first, which we shall refer to as Case 1, the material B can be removed atom by atom until the defining interface is reached. In the second, which we shall refer to as Case 2, one might attempt to effect separation of B and C at the interface only. The particles or "chips" removed, therefore, can range from the dimensions of atoms to the dimensions of the bulk raw material B to be removed.

In considering Case 2, an elementary but nevertheless important difficulty is recognized: that of extricating C from the surrounding material B. This obvious but far from trivial point immediately reveals the topological

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nature of the problem and suggests also why most processes are complex. Either a new surface must be created by cleaving the shell B into two halves, or a "tunnel," large enough to allow C to be extricated from the surrounding material, must be made from the environment E through B to C. Such a tunnel could be produced either by removing all the material filling it or by producing a fissure which is subsequently enlarged by deformation of the material in B. A typical form for such a fissure would be a "half-plane" passed through B and brought into contact with C. Region B could then be opened back on a "hinge" like a bi-valve mussel.

Thermodynamically, the ideal removal process requires an amount of energy equal to that of the new surface created, provided no other energy-absorbing mechanisms are involved. The surface in question includes the interface bounding the configuration plus any increase in surface incurred in extricating the part from its surround. Energy may also be absorbed by plastic deformation, if that is part of the mechanism employed in removing C from B.

Though it is realized that the criterion of minimum energy may, in many instances, be superceded by practical considerations such as tool wear, it is instructive to examine the energy balance of an ideal material-removal process. This ideal removal process may be regarded as that process which, with minimum energy, produces the required new surface bounding the part and leaves the part accessible to the environment.

The upper bound for the energy required in a material-removal process can be estimated from the lattice energy of the material. For example, suppose the excess bulk material B in Figure 3 is removed by vaporization. The energy required is found by multiplying the weight of material to be removed by the lattice energy for the material involved.

As an example consider Figure 4. From the center of a 3-cm cube of iron it is desired to cut a 1-cm cube. (We specify "from the center" only as part of the hypothesis, not for practicality.) Iron has a binding energy of 393,500 joules/mol. Therefore this much energy is required for every mole of iron vaporized in the removal process. In our example 26 cc of iron must be removed, and the necessary energy is 0.4 kilowatt-hours.
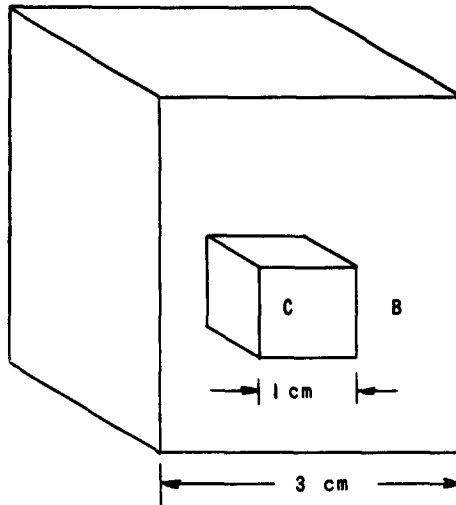
Figure 4   EXAMPLE OF MATERIAL REMOVAL

        Suppose now that we effect separation only at the interface of the
1-cm cube.   A crude approximation might be as follows: Assume that the
removal of a single plane of atoms is sufficient to destroy the cohesion
between B and C, and let it be assumed that these be removed by vaporization.
Since we know the distance between the iron atoms to be 2.28 angstroms we can
find the energy required for the removal of the atom planes again by multiplying
the weight of the material removed by the lattice energy.   The energy required
is less than that required for bulk removal by a factor of 10^{-9}.

        These calculations are not intended to be practical but merely to
indicate the order-of-magnitude differences which can exist between removal
processes in which volume and surface effects, respectively, predominate.
The picture is not greatly affected if one postulates the removal - say -
1000 atom layers rather than a single layer at the interface.   In conclusion,
it is evident that the energy exchanged in a material removal process is
associated with the new surface created.   Thus, to improve the efficiency of
a process, it is essential to improve conditions for utilization of energy at
the interface defining the configuration.

Two general approaches to improving the efficiency of a material-removal process will be discussed.

The first is concerned with reducing the surface energy by environmental means, as, e.g., by embrittlement or by surface active materials which tend to lower the surface energy. How such lowering of surface energy can affect material removal can be appreciated by noting its effect on such phenomena as crack propagation. According to the Griffith concept, for example, propagation of a crack results when the stored elastic energy exceeds the surface energy of the crack. Thus any lowering of the surface energy would tend to favor the propagation of cracks. This approach forms the basis for the concept of embrittlement machining discussed in an earlier report (1).

The second is concerned directly with modification of the geometry or topology of the failure mechanism involved in the removal process, quite independently of the energy conversion system. The principal objective here is to break the minimum number of bonds and yet allow creation of the surface bounding the configuration. The example cited above (Figure 4) exhibits the extremes within which the efficiency of the process can be changed by strictly topological means.

Of the two approaches, it appears that the greatest range of unexploited possibilities may be topological rather than physical. The first approach is mainly one of material modification, whereas the second is mainly one of improving the ability to direct energy, whatever its form, toward the breaking of bonds. In view of the fact that most removal processes are enormously inefficient in the latter respect, we believe that major improvements in material removal might be realized through improved control of processing energy.

In view of the gains that can apparently be realized by topological means, one may well ask whether material removal is really necessary, in the ideal sense, for the fabrication of parts. To answer this question, it is essential to isolate two distinct, though commonly associated, features of most material-removal processes. In general, we think of a material-removal process as some sort of "cutting" process. However, in the ideal

sense, cutting can occur without material removal. This fact suggests that a somewhat more rigorous definition of cutting be provided than that usually held intuitively, and that the conditions under which a cutting operation is necessary be investigated.

In the mathematical sense, the terms "cutting" and "deformation" are defined in terms of topological transformations (2). Let a geometrical figure A be transformed into a figure A' by any correspondence p←→p' in such a way that the correspondence is one to one and continuous in both directions. To every point p of A there corresponds a point p' of A', and vice versa. Further, if two points, p, q of A move so that p ⟶ q, then p' ⟶ q' and vice versa. Such transformations are said to be topological; though they allow changes in the metric and projective properties of the figure, they retain a set of properties called topological invariants. Deformations are an example of topological transformations.

Consider, now, the question of generating new surface in a manufacturing operation. Such surfaces may be characterized, in the topological sense, by the concept of genus. The genus of a surface is the largest number of nonintersecting simple closed curves which can be drawn on a surface without separating the surface into two domains. For example, if a closed curve C is drawn on the surface of a sphere S, that surface is separated into two domains S' and S''. A point p' belonging to S' and a point p'' belonging to S'' cannot be joined without crossing C. Therefore the genus of the sphere is zero. However, a torus has genus 1, because it is necessary to draw two closed curves in order to insure that the surface is divided into two domains. Similarly, a figure like a torus but with p "holes" is said to have genus p.

Consideration of the genus of a surface is essential to a mathematical formulation of cutting. In the mathematical sense (though it may be precluded, of course, by material properties), any configuration of genus p can be transformed by deformation into any other configuration of the same genus. For example, a cone can be deformed into a sphere, a cube, or a cylinder. Such a simple configuration as a flat washer, however, cannot be produced by deformation alone and requires cutting, in

the sense defined above. Therefore, cutting is seen to be an operation which is essential any time the genus of the surface is increased in going from one state in the manufacturing process to another. Conversely, in the reverse process, in which one goes from a configuration of higher to lower genus, the inverse of the cutting operation - that is, joining - must occur. From the mathematical point of view, therefore, a process might be classified according to whether it does or does not belong to the class of deformation processes. Note that such classification emphasizes the topology of the transformation, rather than the metric properties of dimensions or whether volume is gained or lost in the process.

In the mathematical sense, deformation can mean a scalar transformation. For example, in two dimensions, one can consider a figure drawn on a rubber sheet, which can be stretched to expand or contract its size. In physical reality, however, volume changes by shrinkage or expansion are limited; consequently, cutting (or its inverse, joining) must often be invoked to adjust dimensions of the piece. It is in this sense, of course, that cutting processes are regarded as material-removal processes.

In conclusion, cutting operations are required in manufacturing for two reasons: (1) to permit transformations in which the genus of the surface is changed, and (2) to permit dimensional adjustments of the piece.

3.2 Process Synthesis

In Figure 2, the interrelations of mechanical, chemical, thermal, electrical and magnetic energy in all manufacturing processes were displayed as a partially ordered system. In the following discussion, examples are presented of the application of principles of process synthesis to material removal processes in several energy categories.

3.2.1 Physical Models and Their Process Implications

In the past, many physical models have been proposed to represent the mechanical properties of solids and fluids. Each of these models, in addition to its ability to represent the observed behavior of materials, carries implication for certain other postulated properties.

Thus one procedure for the postulation of new processes consists of exploring the implications of such models for new process concepts. In the following discussion the analogs of elastic and plastic material behavior, response to vibratory inputs, relaxation and resonance are explored.

3.2.1.1 Macroscopic Models

In a model for mechanical properties of metals described by Stulen (3), the mechanism of slip is simulated by a large number of friction surfaces having the characteristic of Coulomb friction. The force must reach some threshold value before the surfaces will move relative to each other. A plausible development of the stress-strain curve is then based on the assumption that as the stress is increased an increasing number of slip surfaces is activated.

It is assumed that the rate of change of the number n of slip surfaces with respect to the stress σ is proportional to some power of the stress:

$$\frac{dn}{d\sigma} = b\sigma^{\alpha} \tag{1}$$

The rate of change of strain with respect to stress, $\frac{d\epsilon}{d\sigma}$, is the compliance. If each slip surface has a flexibility a, then the rate of change of compliance with respect to stress is

$$\frac{d}{d\sigma}\left(\frac{d\epsilon}{d\sigma}\right) = a\frac{d}{d\sigma}\left(\frac{dn}{d\sigma}\right) = ab\sigma^{\alpha}$$

or

$$\frac{d^2\epsilon}{d\sigma^2} = ab\sigma^{\alpha}. \tag{2}$$

On integrating (2) and applying the boundary condition that when $\sigma = 0$, $\epsilon = 0$, one obtains

$$\epsilon = a_0\sigma + \frac{ba}{(\alpha+1)(\alpha+2)}\sigma^{\alpha+2}$$

or

$$\epsilon = \frac{\sigma}{E} + c\sigma n \tag{3}$$

as the general form of the stress-strain curve. In equation (3), E is the modulus of elasticity and n^{-1} is the strain-hardening exponent.

Stulen's model is applicable to stress-strain relations that are not time dependent, as, for example, those involved in a slow tension test. When the time variable is introduced, the model must be modified to take into account stress relaxation phenomena and other time-dependent effects.

Fitzgerald (4, 5) considers two general classes of time-dependent phenomena: (1) relaxation and (2) resonance.

In the first case, the frequency dependence of the compliance is analogous to that of the mechanical model of Figure 5. An ideal (massless) spring of modulus G_o and a dashpot of viscosity η_o are in series with a spring of modulus G. The spring of modulus G_o responds instantaneously, but the response of the other spring is delayed by the dashpot with viscosity η . As noted by Fitzgerald, for some cases of relaxation, in materials such as polymers, several retarded spring elements must be invoked to represent the experimental data. The analog of Figure 5 leads to a relation between stress and strain given by

$$\sigma = k_o \epsilon + k_1 \frac{d\epsilon}{dt} . \tag{4}$$

in which the stress is a function of both strain and strain rate.

In the second case, the one which forms the basis of the so-called Fitzgerald effect, an inertial element is added to the model, as shown in Figure 6. Here, the mass of the delayed spring is taken into account, m/ℓ representing the effective mass per unit length of the spring. This model leads to a relation between stress and strain given by

$$\sigma = k_o \epsilon + k_1 \frac{d\epsilon}{dt} + k_2 \frac{d\epsilon^2}{dt^2} . \tag{5}$$

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$$J' = \frac{1}{G_0} + \frac{1}{G}\left(\frac{1}{1+\omega^2\tau^2}\right),$$

$$J'' = \frac{1}{\omega\eta_0} + \frac{1}{G}\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right).$$

Figure 5a MECHANICAL MODEL FOR
RELAXATION DISPERSION

From Reference (5)

Figure 5b FREQUENCY DEPENDENCE OF SHEAR
COMPLIANCE FOR RELAXATION DISPERSION

$$J' = \frac{1}{G_0} + \frac{1}{G}\left(\frac{(1-\omega^2/\omega_r^2)}{(1-\omega^2/\omega_r^2)^2 + \omega^2\tau^2}\right),$$

$$J'' = \frac{1}{\omega\eta_0} + \frac{1}{G}\left(\frac{\omega\tau}{(1-\omega^2/\omega_r^2)^2 + \omega^2\tau^2}\right).$$
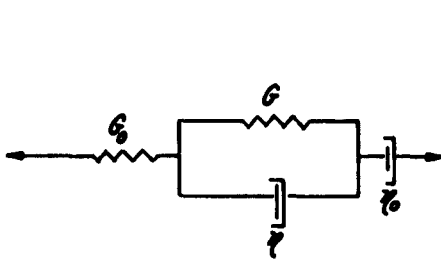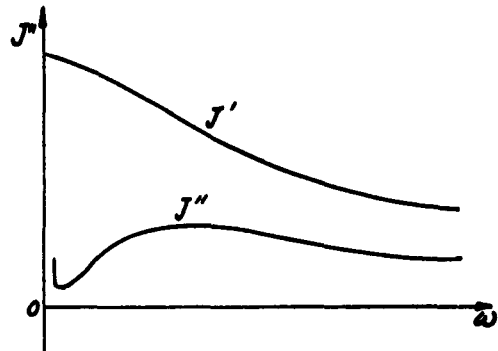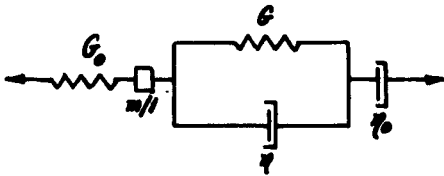
Figure 6a MECHANICAL MODEL FOR
RESONANCE DISPERSION

From Reference (5)
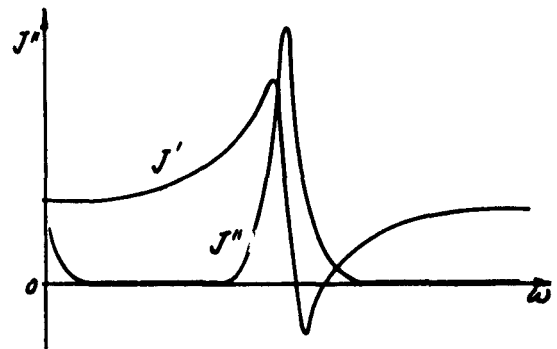
Figure 6b FREQUENCY DEPENDENCE OF SHEAR
COMPLIANCE FOR RESONANCE DISPERSION

Note that the stress is a function of the strain, the strain rate, and the strain acceleration.

Next, Fitzgerald asks what is the frequency response of strain as a function of periodic stress and expresses the results in terms of the complex dynamic shear compliance $J^* = J' - iJ''$, where J' is a measure of the elastic energy stored and recovered during each cycle of deformation and the loss compliance J'' is proportional to the energy dissipated during each cycle. For the relaxation and resonance models, the real and imaginary parts of the dynamic shear compliance are plotted in Figures 5 and 6.

Whether the Fitzgerald effect is useful for purposes of material processing seems to hinge on the manner in which the loss energy is dissipated. Intuitively it might appear that by working at the resonance peak of J'' it should be easier to plastically deform the piece, if for no other reason than that a certain amount of energy has been absorbed and this must in some way lessen the cohesiveness of the material. Attention to J'' suggests, therefore, that the Fitzgerald effect, if existent, has possibilities for augmentation of deformation processes.

There seems to be a difficulty involved, however. Useful exploitation of the energy loss peak implies that additional control forces must be brought to bear on the workpiece, with the result that a transient system of stress is introduced. The results of Figure 6, then, would apparently not be valid unless the composite forcing function were analyzed into its Fourier components and the principle of superposition applied to the spectrum represented by the process. The result will be favorable or unfavorable, depending on the nature of the control forces and the transient response of the system. As a corollary, however, it should be possible to modify the over-all results by varying the wave shape of the periodic stress. Square or triangular waves, for example, would produce effects representing two particular cases of the superposition of Fourier components. In the final analysis, exploitation of the Fitzgerald effect would need to be based on an optimum solution of equation (5) for the combined system of stresses employed in the particular process topology.

Suppose, now, that we focus attention on J', the storage compliance. Changes in frequency of vibration, according to Figure 6, can produce appreciable changes in stiffness. Therefore, sudden changes in frequency should introduce transient phenomena which conceivably could be exploited in manufacturing processes. At a particular frequency J' reaches a maximum and there also exists an optimum frequency at which J'' is substantially zero yet J' is significantly greater than at zero frequency. Suppose a cutting tool is employed at this frequency and is pulsed in such a way that at a selected time the vibrational stress is suddenly removed. The compliance J' then recovers its zero-frequency value, that is, the tool suddenly acquires an increased stiffness and in doing so recovers from the elastic deflection to which it was subjected at the high value of compliance. The result is that the tool delivers an impulse of energy usable in removing a chip from the workpiece. As in the case of deformation processes, of course, the entire stress history must be taken into account in the formulation of such a process, but the concept appears at least as feasible as that of exploiting the Fitzgerald effect in deformation. In particular, the transient response of J' to a step-function change in frequency would need to be known.

Similar attempts might be made to alter the mechanical properties of the workpiece. The nature of the phenomenon, if verified suggests, however, that it may be important to distinguish between vibration-augmented cutting processes in which the tool is vibrated and those in which the workpiece is vibrated. In the latter case one needs to know more about the relation of the Fitzgerald phenomenon to such matters as plastic deformation and fracture. As has been repeatedly noted, ductility is a more critical consideration than economy of energy in a deformation process, and such matters as tool wear may be more important in cutting processes. There is a remote possibility that frequency modification of shear compliance might affect the relative ductility or brittleness of the work material and, if so, might afford a basis for improved deformation and cutting processes respectively.

Fitzgerald's model is new in that it includes an inertial term implying the importance of strain acceleration. This term

implies resonance phenomena. In one of his publications, (6) Fitzgerald even proposes the inclusion of the third time derivative of stress in the stress-strain relation and suggests an antidissipative resonance. This model could be similarly examined for process implications.

From Stulen's time-independent model we have proceeded to Fitzgerald's time-dependent, but steady state, models and finally to the implication that, for process application, transient phenomena must be taken into account. In any manufacturing process we are concerned, for the most part, with irreversible, or at least nonperiodic, disturbances. Steady state is not reached until the end of the process; hence transient phenomena are of primary concern during the formative stages of the process.

3.2.1.2 Microscopic Models

The analogs of Figures 5 and 6 are macroscopic models of the relation between stress and strain; they endeavor to explain the behavior of metals on the scale of a macroscopic sample, rather than on the basis of individual microscopic failure mechanisms. In more detailed models Fitzgerald and others have attempted to treat individual slip planes by the same means; then, assuming either a series or parallel network of elements representing these slip systems, they attempt to derive the response of the entire network (the macroscopic sample) in terms of the responses of the individual network elements. In Fitzgerald's model each slip plane is assumed to behave as a spring-mass-damper dynamic system or as an RLC circuit.

In a broad sense, all such analogs are subject to analysis by means of well-known network theorems capable of providing a considerable degree of generalization (7, 8). Many networks are formally equivalent and it would be a not inconsiderable problem to find all possible equivalents. These methods are basically topological, and employy such concepts as duality* and congruent transformations.

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*In the analysis of networks, one can apply Kirchoff's law either to the voltage drops around a closed loop or to the currents into and out of a branch point or node. Thus if one has a network analog of - say - a mechanical system in terms of voltage, resistance and inductance, a dual network can be derived in terms of current, conductance, and capacitance.

Consider, for example, the problem of synthesizing a four-terminal network having a specified impedance function. Such a network can be realized in a great many ways by various series-parallel combinations of RLC elements. By partial fraction or continued fraction expansion of the impedance function one can find four fundamental equivalent networks for the given impedance function, each network containing a minimum number of elements. These can then be combined in various ways to give further equivalent networks having the same functional characteristics but different physical structures. Further, if L, S, and R denote the inductance, elastance, and resistance matrices of a given network, a real, nonsingular matrix A can be applied to give, by congruent transformation,

$$
\begin{aligned}
\hat{L} &= A'LA \\
\hat{S} &= A'SA \\
\hat{R} &= A'RA
\end{aligned}
$$

where A' is the transpose of the matrix A. L, S, and R are the new inductance, elastance, and resistance matrices for an equivalent network. Though some of these derived networks may not be physically realizable, they can, in theory, be made so by the introduction of one or more ideal transformers to eliminate circuit elements with negative parameters.

The principles of network synthesis are relevant to any dynamic analog of material properties. If the network analog is to be valid in detail then for each element in the analog there must be a corresponding element of similar function in the material. Such material elements might be slip planes, twinning planes, dislocations, etc. If energy is applied to a material in such a way that material properties are changed, the resulting change must be manifested in the model as some nontrivial change in the analogous network topology. On the other hand, it is evident that if the changes are such as to produce an equivalent network, the no change in material properties would be experienced.[*] The

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[*]It may well be that the theory of equivalent and nonequivalent networks may be related to the theory of intrinsic and structure-sensitive material properties.

implication is clearly that many configurations of the actual material elements are capable of giving rise to the same material properties, whereas many other configurations may be associated with modification of material properties. It is conceivable that this feature of the analog may be the formal expression of discrepancies and controversies in the literature regarding theories of material behavior, particularly those dealing with the behavior of materials at high strain rates or under unusual environmental conditions. Since formal procedures are available for deriving equivalent networks, it is conceivable that such derivations, when interpreted in terms of their corresponds in material elements, might shed light on some of the enigmas of material behavior. Further exploration of this approach is planned.

Needless to say, the exploitation of analogs must be approached with caution to insure that there is a real rather than a specious correspondence. The usefulness of analogies resides in the somewhat dubious principle of logic that observed similarities in two systems imply still further similarities, not yet discovered. Thus, in the event that the analog can be more readily manipulated than the system of primary interest, it is possible to make predictions regarding the primary system. The consequences of such logic must then be tested experimentally in the primary system to validate the initial correspondence assumed.

3.2.2 Some Postulated Processes Involving Cavitation

Cavitation is a phenomenon characterized by the rapid or violent formation of vapor cavities in a region of a liquid subjected to very low pressure. Erosion by cavitation is generally regarded as an undesirable effect and usually is studied because its occurrence is to be avoided. In the context of our search for useful material-removal processes a new look at cavitation appears justified. The present knowledge of the phenomenon is outlined in Appendix B and process possibilities are presented in this section.

Cavitation can be induced on the surface of an immersed workpiece by means of the rapid pressure fluctuations set up by intense ultrasonic waves. Ultrasonic waves might be generated by a two- or three-dimensional transducer array whose individual transducers could be

appropriately phased with one another to bring about an enforced wavefront at some spot on the surface of the workpiece. By varying the phase differences between the various transducers in the proper manner, the work surface might be scanned by the cavitation spot. With this type of system a directed and controlled cavitation attack might be carried out by programming the transducer inputs.

Cavitation erosion of metals by pure hydromechanical means is a slow process. However, it appears possible to enhance this effect by varying the physical environment in some manner. Since the rapid collapse of vapor bubbles is basically responsible for cavitation damage, any means of increasing these collapse pressures would increase the material-removal rate. An increase of the static fluid pressure would require ultrasonic waves of higher frequency and intensity with subsequently higher energy densities to bring about cavitation. It is worth investigating whether, with a suitable combination of pressure and ultrasonic frequency, the collapse speed, and thereby the intensity of bubble attack, can be increased. The higher frequency of bubble formation and collapse would lead to more rapid fatigue failure of ductile materials. This effect could probably be optimized by using a degassed liquid at temperatures below those normally used.

High static fluid pressure, in addition to allowing higher cavitation energy densities, can also weaken materials by intrusion as reported by Poulter (9). He observed that fluids with small molecules and low viscosity, such as water, alcohol, and ether, can penetrate solids such as glass, quartz, and metal under high pressure. When this pressure is quickly released the cohesive forces of the solid material are unable to retain the liquid in its compressed state and thus a high internal stress concentration can build up under the surface of the solid leading to failure. The extent of intrusion and the damage that occurs depends on the length of time the material is exposed to the fluid under pressure and the magnitude of that pressure.

Conceptually, cavitation can be combined with embrittlement machining by the use of a corrosive liquid as the cavitating medium. Energy delivered by the collapse of bubbles might then induce brittle failure locally in the workpiece. The degree of embrittlement might be controlled by

controlling the concentration of the corrosive fluid and might be arrested by flushing the workpiece with a second reagent, in much the same way as photographers use a "quick stop" bath in development. To further augment the process, one might combine cavitation of a corrosive liquid with ultrasonic grinding.*

Hydrogen or various other embrittling substances could be dissolved in the fluid under pressure, with the result that intrusion by both the fluid and the embrittling substance would be experienced. The intrusion of liquid and embrittling agent would lower the cleavage stress of the crystal lattice and the surface energy of the material in the vicinity of cracks, thus drastically reducing the resistance of the material to cavitation erosion. In fact, material removal might be achieved with ultrasonic waves of energy densities below the threshold for cavitation.

Finally, the ability of cavitation to work-harden the surface of soft and ductile metals rapidly, may be used to advantage. Thus a controlled cavitation process - even at normal fluid pressures - could be a means of preparing ductile materials for a second process whose removal rate might be significantly affected by differences in surface hardness.

3.2.3 New Chemical Removal Process

In a manner analogous to the preceding postulation of material removal processes based on the usually-avoided phenomenon of cavitation, we have postulated a new chemical removal process based on the usually-avoided phenomenon of spontaneous oxidation.

Spontaneous chemical oxidation is characterized by the liberation of large amounts of heat. In the postulated "combustion machining" processes the rapidity of the reaction and its heat liberation are made "virtues." Oxidation is to be controlled so as to be localized and so as to proceed at a rate intermediate between (slow) oxidation and (rapid) combustion. Control is to be achieved by the suitable combination and application of several energy forms.

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*The importance of cavitation as a process variable in "conventional" ultrasonic grinding will be studied as part of the embrittlement investigation during the next reporting period.

Chemical oxidation energy may be provided by a liquid or gaseous oxygen stream which simultaneously cleans the workpiece surface either through its kinetic energy or through the mechanical energy of grit particles carried in the stream. The gas stream with or without particles, could also serve as the sink for the reaction heat so that the heat affected zone of the workpiece could be controlled. Thermal energy could be further utilized for preheating the oxygen supply or the workpiece so as to speed oxidation rate. Electromagnetic energy may also become a process element. For instance, electric sparks, laser beams, or electron beams might be employed for local ignition of oxidizing material previously applied to the workpiece in a liquid or solid.

The feasibility of this new chemical process is discussed in Appendix A.

4. MATERIAL ADDITION PROCESSES

4.1 General Considerations

The changes in surface area which a material undergoes during a manufacturing operation are related to the topology of the manufacturing process. For example, material-separation processes always involve an increase in surface area, and the theoretical minimum amount of energy absorbed is directly proportional to the new surface created. Conversely, material-joining processes always involve a decrease in the total surface area of the material, and an amount of energy proportional to the decrease in area is given off in the process.* The fact that energy must be supplied in most practical joining processes thus appears paradoxical.

The paradox is resolved by noting that surfaces to be joined, under ordinary environmental conditions, are seldom in a state conducive to the release of energy by surface elimination. The surfaces to be joined usually are covered by oxide layers or other impurities which inhibit the molecular bonding process, and energy must be expended to condition the surfaces so that favorable bonding conditions are realized. No small part of this energy is used in removing the contamination from the active sites where bonding occurs. This part of the process involves either material removal or material deformation to produce sufficiently intimate contact for joining to occur.

Once contact conditions favorable to joining have been attained, the energy-release mechanism dominates the process. Unless the energy released can be removed from the interface, joining cannot occur. For instance, consider the growing of crystals from material in the vapor phase. Initially, energy had to be supplied to vaporize the material involved, but condensation of a mandrel of the desired shape can occur only if the "heat of sublimation" is removed from the vapor to be condensed. The lack of practical means to remove this energy rapidly and under close control constitutes a present limitation on many of the so-called "direct deposition" processes.

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*The correlation of energy release and surface elimination is clearly demonstrated in the spontaneous welding of two pieces of steel under ultra-high vacuum ($\sim 10^{-12}$ Torr).

Material joining processes can be divided into two classes according to the number of units sustaining a reduction in surface area during the process. If the number is large, and the parts to be joined relatively small, the process can be called particle-compact. Typical examples are sintering, vacuum evaporation, ion beam deposition, and electroplating. If the number is small, and the parts to be joined relatively large, the process can be called component-compact. Typical examples are welding, riveting, cementing, and diffusion bonding. In both categories, the various classes of energy - mechanical, chemical, thermal, electrical, and magnetic - and their various combinations are applicable.

4.2 Control Mechanisms

The factors which provide control mechanisms for material-joining processes are the same factors which make the joining operation possible, namely, surface preparation and energy transfer. For example, joining at a given site on the interface between two parts can be encouraged or discouraged by removing or applying a foreign substance which acts as a mask or barrier to prevent intimate contact of the mating surfaces at that site. Alternatively, local environmental conditions either favorable or unfavorable to energy transfer from the site can be provided. For example, in the discussion of shape control in vapor deposition processes, in Appendix C, it is shown that the temperature of the substrate can be varied to control the rate of deposition over the depositing interface.

4.3 Process Synthesis

As an example of the synthesis of a material-joining process, consider a component-compact process utilizing chemical energy. The chemical energy is applied in such a way as to remove impurities and promote interfacial contact, as, e.g., by dissolving unwanted surface films. Other forms of energy may then be required to insure success of the material-joining operation. For example, it may be necessary to remove the chemical agent with its dissolved impurities by mechanical means and possibly apply heat to diffuse the remainder of the agent away from the joint.

Heat - and possibly pressure - might also be required to promote plastic deformation so that any remaining surface irregularities could be eliminated.

Conversely, we may conceive of an entire category of joining processes based on the addition of a liquid medium between the mating surfaces. For example, mercury and gallium are liquid metal "solvents" which can aid in joining metals, as, e.g., in dental alloys. More correctly, the liquid metals in this case constitute the matrix of a mechanical mixture or suspension of the particles to be bonded. The liquid metals diffuse into the base material as bonds form and the compact hardens, and the resulting interface may show little of the "solvent" phase upon curing. The resulting joints thus have the strength of the base metal and are not limited by the strength of the matrix, as is the case with conventional solder. The concept can be extended to other materials which are liquid only at elevated temperatures. The practice of soldering or brazing two tungsten pieces with the aid of a thin film of nickel which is later diffused into the tungsten by heat treatment may serve as an example. Similar schemes appear possible for joining ceramic materials.

In view of the fact that surface preparation is an important part of the joining process, an unconventional approach to joining is suggested by modification of the process topology. For example, if two pieces of material are to be joined over some interface of area A, it may in some cases be more feasible to minimize the area over which bonding is promoted. In this way the necessity for cleaning a large area is eliminated. Provided that the material is capable of undergoing appreciable deformation without fracture, the desired configuration could then be developed by a suitable deformation process. In such a combined process, the joining operation is used only for effecting the required change in genus of the surface, as described in Section 3.1, and continuous deformation is relied upon for developing the desired geometry.

5. MATERIAL DISPLACEMENT PROCESSES

5.1 General Considerations

Topologically, displacement processes are those in which the geometric shape of the material is changed but the genus of the configuration remains invariant.

From the topological and physical aspects of the process it follows that practically all displacement processes involve a change in the magnitude of the surface area, although, theoretically, a displacement process resulting in a zero net-change of surface area is possible. It also follows that in displacement processes the distance between points in the interior and on the surface of the workpiece will change. Examination of possible mechanisms for changing these distances is therefore relevant to the synthesis of new displacement processes.

Examination of the inherent energy requirements of displacement processes is also pertinent. Generally, the energy required will become less as the number of discrete displacements and the distances over which they occur is decreased. Further, environmental factors influence the specific energy required.

In the following section macroscopic and microscopic aspects of plastic flow are discussed.

5.2 Macroscopic and Microscopic Aspects of Plastic Flow

Two primary factors which control plastic flow in a material are its ductility and its strength. Factors included in the study of ductility are the elastic limit, the yield stress, strain, and strain hardening.[*] Ductility is a measure of deformation which can occur before fracture; ultimate strength determines the power required for the forming operation. In general, we would like to improve the ductility of the material and decrease its strength while it is being formed. We also want to maintain or increase the strength of the formed material compared to that of the preformed material.

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[*] A discussion of dislocation theory as applied to these factors appeared in Appendix G of the Third Interim Technical Report, Reference (1).

The energy and environment can be controlled so that the ductility and strength of the material can be varied. The major energy and environmental factors are temperature and strain rate. In general, changes in temperature and strain rate have inverse effects on ductility, that is, an increase in temperature and a decrease in strain rate result in an increase in the ductility of the material. (10) Attempts to explain this behavior in terms of dislocation theory have had considerable success at temperatures above $0.6\ T_m$, where T_m is the absolute melting temperature of the material. At lower temperatures the role of dislocation motion in determining the strength and ductility is not well understood. To understand the factors which control the ductility and strength of materials, we must consider the changes that occur in the structure during plastic flow.

The ductility of materials at high temperatures is controlled by the ease of dislocation motion in the crystalline material, by the manner in which dislocations move, by the ease of twinning, by the ease of grain-boundary shearing and migration, by the rate of atomic mobility and at high temperatures by the ease of recrystallization. For good ductility at low temperatures the metal must deform readily along many glide or slip planes.*

The number of slip planes in a material is a function of its crystal structure and its temperature. Face-centered-cubic (FCC) structures have 12 possible slip directions. Both single crystals and polycrystals of metals having this structure exhibit high ductility which can be attributed to the large number of slip mechanisms available in this crystal system.

In hexagonal-close-packed (HCP) crystals there are three potential slip planes, namely, the basal plane, the prism plane, and the pyramidal plane. Which slip planes are active depends on the metal and temperature. In the basal plane there are three directions in which slip can occur. There

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*A separate report on the application of dislocation theory to deformation processes will be issued in the next reporting period. The material presented in this section is but a brief portion of the forthcoming report and it is used here to illustrate how the synthesis problem might be attacked by considering the effects of changing the material structure.

are three prism planes in the lattice but only one direction of slip in each plane. There are three mechanisms for slip in both the basal plane and the prism planes. In polycrystals slip can only occur in those active planes and in the direction within the planes which are aligned with the stress field. In prism slip which involves nonparallel planes there are three possible planes which can line up with the stress field whereas in basal slip there is only one slip plane; hence prism slip results in greater ductility. There are six slip mechanisms in the pyramidal plane and hence the greatest ductility of HCP structures occurs when slip occurs along the pyramidal plane.

Body-centered-cubic (BCC) crystals have 48 possible slip mechanisms and the ductility of these materials should be extremely high. This is the case if the polycrystalline material is extremely pure or tested at an elevated temperature. However, impurity elements, especially interstitial ones, strongly interact with the dislocations to prevent slip and lead to low ductility. In the diamond structure, slip apparently can occur along the (111) plane but the presence of strong covalent bonds and the difficulty of dislocation motion contribute to its low ductility. At high temperatures and low strain rates dislocation are allowed to climb preventing stress concentration at dislocation pile up.

Because different crystalline structures exhibit different degrees of ductility one approach to improving the formability of a material is to change its crystal structure. Many metals exhibit phase changes as a function of temperature, iron being a common example. For example, low carbon iron transforms from alpha BCC to gamma FCC structure at 900°C and suffers a decrease in ductility accompanied by an increase in strength. Two factors contribute to the decrease: in ductility the major factor is the decrease in diffusion rate of iron atoms on forming the FCC structure, the second factor is the decrease in number of slip mechanisms from 48 to 12. However, the reverse occurs when gamma iron transforms into delta iron which is BCC at 1400°C.

An increase in atomic mobility and in the number of slip planes may not result in increased ductility if slip and deformation are concentrated within the material. For example, when extremely extensive dislocation

motion is concentrated on a single plane, the two halves of the material slip apart without deformation and brittle fracture results. Thus the availability of extensive dislocation motion alone is not sufficient to guarantee ductility.

Uniform distribution of dislocation mobility throughout the metal improves its ductility. The high energy rate processes - which use the energy of an expanding shock wave in a medium such as water to deform a material - have been successful because they produced a more uniform distribution of deformation in the material. There is evidence that the ductility of the material has increased during these processes.(11). In austenitic steel, slip normally occurs on the octahedral planes. In explosive forming, slip has also been observed on cube plane and mechanical twinning occurred. Hence, the high energy density of the shock front activates slip mechanisms which are normally inactive.

5.3   Process Synthesis

Synthesis of new or improved displacement processes can take place on the macroscopic and on the microscopic level.

On the former, we include well-known effects such as reducing friction along tool-workpiece interfaces through the introduction of vibrations or lubricants. Since the formability of many materials is limited by their tendency to fail in tension during deformation, process synthesis should favor the employment of process topologies in which compressive stresses predominate. Therefore, an examination of conventional techniques of wire drawing and swaging, as extremes of operations employing tensile and compressive stresses, respectively, is warranted. The notion of designing a process so as to achieve a stress distribution permitting maximum deformation is, of course, embodied in recent deformation processes using hydrostatic pressure.

On the microscopic level we must examine the methods which increase the number of slip systems in a material, increase atomic mobility, and increase the ease of twinning, as discussed in Section 5.2.

From the standpoint of energy, we will seek combinations (mechanical, chemical, electrical, thermal, and magnetic) which improve ductility. Each form of energy which can bring about displacement can be considered separately. Mechanical energy alone is used in the cold working processes of the metal working industry. Thermal energy only is used in the casting process. Magnetic energy has more recently been introduced to forming operations and is now the basis of commercial process. Forming operations in which electric and chemical energy interact directly with the material do not exist. However, electro-hydraulic forming and explosive forming are examples of newer processes in which these energy forms play a major role.

The most obvious energy combination is the thermal-mechanical subclass, the basis for all hot forming operations. Improvements in hot forming may result by processing certain materials at temperatures below conventional hot forming temperatures.(10). In mild steel, for example, the ductility between 600°and 800°C is equal to that between 1000° and 1200°C. Less heating would be required but an increase in mechanical energy would be needed because the steel has higher strength in the lower temperature range. Thus, though the same amount of total energy would be required in either case, a more favorable substructure would result at the lower temperature range.

Examination of the other combinations of forms of energy as applied to deformation processes is expected to reveal possible new processes. For example, electric fields have been shown to increase the ductility of ionic crystals (11). Hence it appears possible that the combination of electric with mechanical and thermal energy might enhance the formability of the "non-ductile" ionic materials. The systematic discussion of electrical effects in ionic crystals in Appendix D is to lay the ground work for such an effort.

The combination of magnetic and thermal energy leads to the following speculation: The important characteristics of the magnetic forming operation are the even distribution of stresses set up in the part being formed and the high rate of energy transfer to the material. So far magnetic forming has been primarily applied to ductile metals. Consider the possibility of applying magnetic forming to brittle, high strength, non-conductors. First,

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the material can be made conductive by plating or coating a conducting material on the non-conductor. Second, the application of thermal energy could raise the temperature into a range where a structural change occurs which renders the material ductile and ready for magnetic forming. A coil in close proximity to the material usually provides the magnetic energy; it is possible that the same coil could be used for induction heating of the material. Additional power supplies would be necessary since induction heating requires an alternating current whereas magnetic forming requires a short duration high energy pulse.

6. PROGRAM FOR NEXT PERIOD

During the next 6-month period the emphasis of the project effort will continue to be placed on process synthesis. In addition, effort now under way will continue in the following specific areas:

Embrittlement machining experiments, designed to test the principles and applicability of material modification schemes enunciated earlier (1, 11), will be performed at MIT and THERM Inc. under subcontract.

We will continue an investigation, currently under way, on the effects of high power, high frequency electromagnetic radiation on materials.

A survey program concerning dislocation theory and its application to displacement processes will be completed and released as a special report.

Feasibility studies will be made of new concepts such as the processes based on cavitation and on rapid oxidation which were presented in this report.

APPENDIX A

CHEMICAL MATERIAL REMOVAL PROCESSES

In parts A-1 and A-2 of this Appendix, the state-of-the-art of chemical material-removal processes is briefly reviewed and areas in which the potential of these processes is not fully developed are indicated. In part A-3 a new chemical removal process is described and its investigation is recommended.

Individual chemical material-removal processes are called variously chemical machining, etching, chemical milling, electrolytic grinding, electrolytic machining, and others. However, these processes and their subvariations really differ only in detail and technique. They share the essential chemical feature of oxidation.*

If no interfering (impermeable) product layer develops, the rate of solution (oxidation) of a metal in a reactant solution will be determined by: (1) the rate of transport of fresh reactant to the metal surface, (2) the rate of transport of products away from the surface, or (3) the rate of reaction at the metal surface. (1) and (2) are subject to control largely by mechanical agitation of the solvent; i.e., rather than relying on natural diffusion of products and reactants, flow may be forced. The reaction rate of reactants once they are brought in contact, is highly temperature dependent because an activation energy is involved and the percentage of reactant ions, atoms, or molecules having the necessary activation energy increases very rapidly with temperature. A two-to-fourfold increase in reaction rate frequency accompanies a 10°C rise in temperature.

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*Oxidation of a metal, as well as any reaction in general, will take place under circumstances such that the free energy of the products formed is less than that of the reactants, provided that there is not physical interference. Chemists regard the change of a neutral metallic atom to an ion in solution or compound as oxidation. In terms of the exchange in electrons, oxidation means the loss of one or more electrons from each metal atom, leaving a surplus of positive nuclear charge over the aggregate negative charge of the orbital electrons. Thus the combination of iron and oxygen to form iron oxide is oxidation as such, and the solution of metallic iron in an acid to form ions is oxidation by analogy.

An important feature of oxidation occurring spontaneously (without externally supplied energy) is the evolution of heat associated with the decrease in free energy of the system.

A-1 Non-Electrolytic Chemical Removal

Chemical milling and etching are the terms commonly applied to the simple chemical oxidation of metals without externally supplied electrical potential. Suitably masked objects are, in the simplest case, immersed in an acidic. or alakline solvent solution and bath temperature and time are controlled. When interfering product layers are encountered, changes in solvent formulation which will eliminate the layer are sought. Gentle agitation may be used.

Removal rates in chemical milling are slow; a rate of 0.010" per minute is considered high. Removal rates are improved by spray and splash application of the solvent, while dimensional control and good surface finish are maintained. The flowing solvent removes both reaction products and the reaction heat more efficiently than does a nearly quiescent bath. Stationary chemical gels have also been considered as removal agents (12).

Because removal rate is slow in chemical milling, that process has been relegated to the specialized areas of printed circuit work, sheet thickness reduction, over-all weight reduction, and production of thin parts normally produced by punch-press operations. However, it appears that the real limitation is not imposed by available reagents or techniques, but by the fact that dimensional control and surface finish tend to degrade rapidly when removal rate is increased. The underlying cause of this degradation is believed to be the following: material removal is essentially atom by atom, and the heat released upon oxidation of each metal atom is large; accelerated rates therefore lead to local accumulation of heat on both micro- and macroscopic scales. Despite the relatively good efficiency of sprays or splashes of solvent in removing heat, localized heating results in local increases in reaction rate, and dimensional and surface finish control are lost.

Improvements in masking, bath formulation, agitation, spraying and splashing equipment will no doubt continue to be made. However, the aspect

of the chemical milling process where there is the most urgent need for a drastic improvement seems to be in removal rate. Because controlled removal rate is limited by reaction heat accumulation and localization as indicated above, we must search for methods to reduce heat liberation.

Unfortunately, fast reaction rates usually go hand in hand with large amounts of reaction heat. One possibility for the reduction of the ratio of heat liberated to metal volume removed appears to lie in removing <u>blocks</u> of metal along boundaries rather than atom by atom, as indicated in Section 3.1.

A possible method for removing the liberated heat is to allow the reaction products to undergo an endothermal reaction with an added species. In the case of oxidizing a metal at a wall, the reaction product might be allowed to undergo the endothermal reaction right at the wall and hence liberated heat would be eliminated on a differential scale. A search for suitable endothermal reactions appears worthwhile.

Conceivably also, material can be modified by providing a grain boundary phase which is much more rapidly dissolved than the bulk of the grains. Such a modification is within the realm of the possible, but probably most alloys could not be so modified without degradation of strength properties.

A-2   Electrochemical Processes

Electrolytic grinding, machining, or etching are the terms applied to processes involving a conductive electrolyte solution, a stationary or moving conductor to serve as a cathode, and a conductive workpiece. The workpiece is made anodic by application of an electrical potential of proper magnitude and polarity. Oxidation of surface metal atoms to positive ions occurs at the anode, and reduction of a positive ion (metal or hydrogen) takes place at the cathode.

Probably the most important difference between chemical oxidation and electrochemical oxidation is that in the latter a potential is applied so as to force the reaction to proceed in the direction of free energy <u>increase,</u>

so that electrical energy is absorbed rather than heat being liberated. (Some heat will be liberated by secondary reactions.) The difference in electromotive potential between anode and cathode determines the magnitude of the free energy increase; if anode and cathode are of the same material, the free energy remains constant.

Anodic solution products of metals tend to be stable, protective films, often oxides such as those formed on anodized aluminum. Such films "physically shield" the anode and must be removed. Removal can be accomplished in a number of ways, e.g., by making the bath capable of chemically dissolving the film, by periodic reversal of polarity, or by ultrasonic agitation (13). In the "electrolytically assisted" grinding process, the film is removed mechanically through a metal wheel or conductive-bond abrasive wheel. The low wear rate of the abrasive wheel in such machines indicates that stock removal is roughly 95 percent by the electrolytic action (14). Of course, the use of mechanical film-removal changes the nature of the process from one where all unmasked surfaces are attacked to one in which the profile of the tool is reproduced as in ordinary grinding or milling. Faust, et al. (15) used very high speed metal wheels, apparently accelerating the electrolyte to a velocity at which it was able to remove polarizing films.

The important limitation on electrochemical processes appears to be removal rate, which is determined by surface finish, dimensional tolerances and by the current-carrying capacity of the electrolyte. The amount of metal removed is inherently proportional to the current density, and spark discharges through the electrolyte begin at some limiting current density. We conclude that electrolyte modification and methods of heat dissipation are the most important areas for research in electrochemical material-removal processes.

A-3   A New Chemical Removal Process

   A-3.1   The Mechanism

As discussed in Section A-1, chemical oxidation is accompanied by the liberation of large amounts of heat when the reaction proceeds spontaneously. In this section we will describe a novel process, the feasibility of

which has not yet been determined, which takes advantage of the spontaneity and heat liberation of oxidation reactions in a rapid "combustion machining" process. In its most crude form, such a process might consist merely of an oxygen torch with which a preheated metal could be caused to melt and burn locally and thus be cut as desired. However, a much more subtle and controllable combustion machining process can be envisioned.

Before outlining the proposed process, it is necessary to discuss briefly the ignition and combustion behavior of metals, and to present examples of uncontrolled metal ignition.

Combustion may be defined as the rapid combination of a material and oxygen, with the production of heat and light. Direct combinations with oxygen result in heat liberation as shown in Table I (16).

TABLE I

HEAT LIBERATED IN DIRECT COMBINATION WITH OXYGEN

Metal	Heat of Combustion (Approx.) Kcal/gram	Btu/pound
Aluminum	7.4	13,000
Zirconium	2.8	5,100
Thorium	1.3	2,300
Iron	1.7	3,000

For combustion to continue at the surface of the metal, it is necessary that oxygen be supplied at a sufficient rate, and that combustion products (oxides) be removed from the burning "zone" rather than being deposited on the metal surface.

Ignition may be defined as the transition from slow, isothermal surface oxidation to rapid combustion. The features of the ignition process are variable, complex, and poorly understood (17, 18). In general, ignition occurs when the heat flux to the surface of a metal due to oxidation and to any externally applied heating becomes greater than the heat losses from the surface by all means (convection, radiation and conduction). Under these

conditions ignition occurs because the rate of oxidation increases with temperature, and an infinitesimal increase in temperature above the balance point results in a "runaway" increase in oxidation rate due to self-heating.

A number of "unpredictable" ignitions have been noted in the literature.

Workers in rocket development have found that metals can react violently with LOX (liquid oxygen). Titanium alloys are particularly sensitive (19). In one case, titanium tubing containing LOX at 700 psi ignited and burned. In another case, a titanium alloy pressure vessel exploded after filling with LOX. Experiments indicated that the reaction with LOX depended upon the presence of two conditions namely, a "fresh" metal surface, and pressurized gaseous oxygen actually in contact with the fresh surface. These conditions could be provided by impacting a surface in contact with LOX. Impacts of the order of 70 ft-lb/in^2 were sufficient to cause reaction. It was speculated that the low thermal diffusivity of titanium was responsible for the ease of ignition. However, other metals ignite in LOX at higher impacts. A standard test consisting of 20 impacts at the 70 ft-lb/in^2 level is employed to screen metals suitable for use with LOX.

Many metal powders are easily ignited. According to Conway and Grosse (21), ignition temperature (in air) of a group of powders were as follows: Iron - 315°C, manganese - 450°, silicon - 775°, copper - 700°, thorium - 270°, zirconium - room temperature. Littman, et al. (21) found that titanium and zirconium in rod forms will ignite when sudden exposure of a fractured surface to oxygen under pressure is achieved. Pressures between 350 and 1000 psi were required. Ignition of oxide-coated zirconium was obtained in shock-tube experiments, indicating that shock waves can remove oxide protection.

If oxidation rate (and therefore oxidation heating rate) were a function of temperature only, the onset of ignition in the above cases would be completely predictable. However, oxidation rate is also a function of the thickness and permeability of the oxide layer existing on a metal at any instant. Rapid oxidation and ignition are favored by the following:

1. Sudden introduction of heat to a cool surface having only a thin, room temperature oxide coating.

2. Sudden introduction of oxygen to an object heated in a nonreactive atmosphere.

3. Forcible removal of protective oxides by mechanical contact or by gas flows capable of exerting large stresses.

A-3.2 Process Possibilities

Controlled rapid material removal might be achieved without overheating the workpiece to an appreciable depth, if surface oxidation can be localized and held at a rate intermediate between slow oxidation and combustion. The necessary conditions might be satisfied by a high velocity stream of liquid or gaseous oxygen carrying solid particles, e.g., oxide grits, as follows:

1. The grit, upon impacting the metal surface, would create fresh (unprotected) areas for reaction. By giving up kinetic energy to the metal the grit would also heat the fresh metal area causing the oxidation reaction to proceed more rapidly. The contribution of impact energy in this fashion probably is not major.

2. The liquid or gaseous oxygen, supplied at whatever velocity and pressure found necessary, would provide an abundant supply of reactant and in conjunction with the grit, would carry away the metal oxide product. Much of the exothermic reaction heat might also be carried away, so that the conduction of heat into the workpiece would be minimized.

3. Areas not directly impinged upon by the grit would remain protected by an oxide layer, and would not oxidize further so long as their temperatures were moderate. The flowing oxygen might act as a coolant in these areas to help localize material removal. This factor together with continual movement of work relative to the stream (as in conventional single-point cutting) might assure that good dimensional control and little subsurface damage would be obtained.

4. Where necessary, preheating of the workpiece and/or a gaseous oxygen supply would be provided to speed oxidation rate. Of course, if excessive preheat is applied, control will be lost and the process will be merely oxygen torch cutting.

Variations in all elements of the process outlined above are possible; in fact the scheme presented should be considered only as one of several approaches to implementing the idea. For example, it might be possible to dispense with any grit or mechanical contact with the work surface by employing an oxygen gas stream of very high velocity. The kinetic energy of the oxygen molecules impinging on the work surface might be made great enough to provide the protective oxide removal and local heating functions thought to be required. An assessment of the energy transfer problem and the gas velocity requirement will be made.

Another rather distinct path of approach lies in the use of solid oxidizers in the form of compounds. Explosive primer technology would be applicable in this area. For example, the workpiece might be coated with a film of oxidizer or primer material so that an energy source such as an electric spark, laser beam, or grit stream would cause localized ignition and material removal when properly applied. A moving sheet or "tape" of oxidizer might be employed in such a way as to make the process continuous. It should be possible to control propagation by proper formulation of oxidizer or primer materials. The start and rate of reaction propagation may also be controlled by the use of sensitizers, a technique well known in the explosive industry.

A stream of solid oxidizer rather than LOX or gasous oxygen would be a further general variant of the proposed process. Solid oxidizers with energy storage capabilities equaling that of liquid oxygen are available.

On the basis of our very brief study, it is difficult to predict whether or not the process would be limited to a few highly reactive metals. The reasons for the reactivity of titanium and zirconium, as outlined above, are not well understood and there seems to be no fundamental reason why these two metals should be unique in oxidation behavior. Thus the process might be very widely applicable.

We conclude that the feasibility of combustion machining should be investigated experimentally. In view of its attractiveness, in principle as a manufacturing process of large material removal capability independent of work material strength, we plan a vigorous follow-up.

We realize that control over the process may be difficult to achieve. The existence of hazards in the use of pure oxygen in liquid or gaseous form is also recognized. However, the methods of handling LOX have developed greatly in recent years, so that both experiments and practical development of a process will be feasible.

APPENDIX B

CAVITATION

New manufacturing processes involving cavitation were outlined in Section 3. 2. 1. 2. In this appendix we review the current understanding of the cavitation phenomenon and of the damage mechanism.

B-1 The Phenomenon

Cavitation is a phenomenon characterized by the rapid or violent formation and collapse of vapor cavities in a region of a liquid subjected to very low pressure. First encountered in connection with high speed propellers, cavitation damage or erosion can take on serious proportions. For example, there have been cases in which transatlantic ocean liners have required propeller replacement after only two round trips across the Atlantic; under critical circumstances high-speed propellers have eroded in a matter of hours (22).

Because of its similarity to the normal boiling of a heated liquid, cavitation is often referred to as a "cold boiling" effect. It can also be referred to as the breaking or rupture of a liquid under tensile stress. For most engineering problems cavitation may be expected when the local liquid pressure drops to the vapor pressure of the liquid at that temperature; however, the actual local pressure at which cavitation begins may be above or below the vapor pressure depending on the gas or solid matter content of the liquid (23). This behavior can be more clearly understood when the concept of bubble nucleation is considered.

There is little doubt that cavitation of a liquid under reduced pressure or boiling of a heated liquid begins with the growth of microscopic vapor or gas nuclei (23, 24). The importance of gas nuclei is brought out by the fact that clean, degassed liquids will not rupture or begin cavitation until the liquid pressure drops well below the vapor pressure. In fact, for water this pressure difference may be as much as the equivalent of 6 feet of water (23, 25). It is estimated that the critical size of the vapor bubble nuclei required to

start cavitation in degassed water is no less than 10^{-5} cm. On the other hand, water with a high dissolved-air content can begin cavitating at pressures equivalent to 5 feet of water above the prevailing vapor pressure. In this case, the bubble nuclei contain mostly air. It has been observed that only the large air bubbles (approximately 0.02" dia.) become unstable and grow, thus initiating cavitation; smaller ones (approximately 0.002" dia.) remain stable until much lower pressures are reached (26).

A distinction between two types of cavitation can now be made. One type (vaporous cavitation) involves a liquid and cavities containing only vapor. Gaseous cavitation on the other hand, involves a liquid containing dissolved gas so that bubbles are first formed by outgassing of the liquid at pressures above the vapor pressure. This latter case is the most prevalent since, in practice, water usually contains dissolved gases such as N_2, O_2 and CO_2. Because of outward gas diffusion, bubbles formed in gaseous cavitation soon contain mostly vapor. This vapor bubble is not dynamically stable, and when disturbed, it may collapse or grow rapidly depending upon its size (25).

Cracks and crevices in hydrophobic boundary material are the most probable source of macroscopic gas nuclei, although small undissolved foreign particles entrained in the fluid may also have small volumes of undissolved gas associated with them. These small, undissolved, gas volumes trapped in boundary crevices can grow at sufficiently low pressures, and upon reaching a critical size they can become unstable, grow rapidly and nucleate the cavitation process (26). It is also possible that under flow conditions the pressure within crevices may be lower than at the surface, thus increasing the possibility of gas or vapor bubble formation.

It might be suggested at this point that the relationship between bubble nuclei and the rupture of a liquid is somewhat analogous to the relationship between imperfections and the tensile failure of a solid.

B-2   Cavitation as a Source of Damage

Cavitation damage appears to occur only as the result of bubble collapse, although collapse need not occur at the surface to cause damage. As Hall and Ackeret have shown, shock waves alone can produce surface damage. The

pressure shocks required to produce erosion were surprisingly low inasmuch as pressure impacts of the order of 0.21 to 0.35 lb/in^2 were enough to attack soft materials like aluminum alloys, copper and pure iron after 100,000 to 200,000 impacts. Harder materials such as steel required only an increase in the number, but not in the intensity, of impacts (27).

Although the exact manner in which the collapsing bubble interacts with the surface has not been fully resolved, it seems certain that cavitation erosion depends on the magnitude of the pressure impulse of collapsing bubbles in some direct manner. Therefore, it may be helpful to discuss the theoretical and measured values of the pressure developed by collapsing cavities. It is difficult to devise a theoretical model which will allow a complete description of the process of cavity collapse and thus make possible an exact calculation of collapse pressure. Most theoretical treatments of bubble collapse assume that the bubble cavities are perfectly spherical and that they collapse concentrically. The following theoretical results reviewed by Eisenberg (23), serve to illustrate the ideal upper and lower limits of collapse pressure.

Rayleigh's treatment assumed an empty cavity whose wall motions were governed by the inertial effects of the liquid. This treatment leads, however, to infinite collapse pressures. A later calculation by Silver assumed that the rate of collapse depended entirely on the rate at which the vapor in the cavity condensed. Although Silver's calculation ignores many effects, it is thought to represent at least the lower limit of the pressure pulse of a spherically collapsing cavity. This limit is on the order of tens of tons per square inch, the approximate order of magnitude for fatigue failure of cast metals. High-speed bubble photographs taken by Mueller indicate that the bubbles do not collapse spherically concentric but are longitudinally flattened. Theoretically, the change in mode of collapse should lead to pressure impacts of only a few hundred atmospheres or a few tons per square inch. Pressure pulses of this magnitude have been indicated directly with piezoelectric gauges although accurate measurements of these transient pressures have not been made (27, 28). Thus, the present understanding of cavitation damage indicates that the pressures due to bubble collapse might be too small to account directly for most cavitation damage (23).

Cavitation erosion was first noticed as a form of pitting attack similar in some respects to chemical corrosion. However, in addition to the honeycombed, pitted effect, there was also evidence of deformation of the metal surface (28). Although the predominant effect responsible for cavitation damage is generally believed to be hydromechanical (erosion) as opposed to chemical (corrosion), the two effects can occur together with the proper materials and conditions and are difficult to separate. These two effects can support each other in the following ways: the mechanical effect can remove a thin, protecting oxide layer leading to more rapid corrosion, and a corroding effect can decrease the fatigue strength of the material's surface and thus lead to more rapid hydromechanical erosion (27). If obviously corrosive conditions are eliminated, cavitation damage seems to be the result of purely mechanical action leading to eventual fracture of brittle materials and fatigue failure of ductile materials (23).

Brittle materials such as strain-free glass can be damaged rather quickly by cavitation, and upon examination cracks are found in the interior about 0.05 to 0.2 mm below the surface (27). Ductile materials exhibit more complex effects when subjected to cavitation. There is evidence of plastic deformation effects such as rapid work hardening, crystal sliding and twinning, and intercrystalline cracking (28, 29). Fatigue failure, already mentioned in relation to damage of ductile materials, has been identified in cases where the failure occurs beneath the surface in a previously stressed zone. The resulting cracks are typical of fatigue or cleavage. Also, the induction period found associated with cavitation damage generated by ultrasonic means has been correlated with the fatigue limit of some materials (28). In general, once cracks are formed, erosion is accelerated - probably because high stresses can be built up at the bottom of cracks and crevices. In this case, large pieces of the surface material may separate because of structural weakening in the vicinity of cracks.

There is an important relationship between the hardness of a metal and the extent of cavitation damage: the erosion resistance of most metals increases almost directly with hardness. Many soft materials such as stainless steel seem to show effects of work hardening and subsequent erosion resistance (28). Grain size has a very significant effect on the erosion rate;

it is found that among metals of similar hardness, the coarse-grained samples erode faster than the fine grained. The effect of inclusions in cast metals is very pronounced. In fact, the erosion attack occurs primarily at the inclusions, which action leads to rapid weakening and removal of large pieces of the metal. Iron with graphite or slag inclusions provides a good example of such rapid erosion (30).

Although properties of the fluid and its condition obviously have a marked effect on the inception of cavitation, they also appear to have effects on cavitation damage. A high dissolved-gas content leads to lower erosion rates, probably because bubbles with a high gas content collapse more slowly than do pure vapor bubbles and subsequently produce smaller pressure shocks. Also, the presence of small gas bubbles on the material is known to have a cushioning effect, and, in experiments in which gas bubbles were injected into the cavitating regions, damage was drastically reduced (28).

An influence of temperature on cavitation damage in sea water has been observed. Between 0°C and 50°C the erosion rate approximately doubles; with the maximum rate occurring at 50°C; upon further increase in temperature the damage rate approaches zero at the boiling point. This variation is probably due to the overlapping of two effects; that is, from 0°C to 50°C the dissolved air content is progressively reduced, leading to higher bubble-collapse impulses, but above 50°C the increase of vapor pressure with temperature is predominant and leads to lower collapse pressures (28).

In summary, although many mechanisms have been proposed to explain and describe cavitation erosion, it is generally agreed that the damage is directly associated with the pressure impulses arising from bubble collapse. Whether these pressure impulses lead directly to fatigue failures or to crystal deformations that may result in piezogalvanic corrosion is still not resolved to everyone's satisfaction. Since the cavities do not collapse in a spherical mode, it is not clear that the cavity collapse shock alone is always sufficient to cause damage. Eisenberg has suggested that a small re-entry-type liquid jet may be produced by the nonspherical collapse of cavities on the surface of the material, thus leading to a possible water impingement attack on the surface. (23) Ellis and co-workers using photoelastic techniques

seem to have demonstrated the existence of a jet formed in a bubble during
nonspherical collapse. (30) Liquid jets have been shown to produce erosion
damage which is very similar to that produced by cavitation; the dependence
on surface and material properties such as hardness, grain size and inclu-
sion similar in both cases. (27)

Even though piezoelectro chemical mechanisms are not generally
thought of as being primarily responsible for cavitation erosion, it is known
that stress corrosion effects can become very important under the proper
conditions. Since, in practice, water containing an electrolyte is often the
cavitating medium, stress-corrosion mechanisms will always remain a
tempting explanation for cavitation erosion.

APPENDIX C
SHAPE CONTROL IN VAPOR DEPOSITION

The intriguing prospect of achieving a design configuration in a differential or atom-by-atom fashion has been pointed out as representing an ultimate in material manufacturing processes.(11). Direct deposition methods, the resulting material properties, and configuration control prospects were categorically discussed.(1). In this Appendix we present ideas on shape control in vapor deposition that are the result of but a brief study. Much of the material is tentative and may not stand up under detailed analysis. In presenting the ideas in their present form we endeavor to (1) illustrate methods for process synthesis and, (2) spark further development in this important area by others.

Control of growth conditions can be exercised through: (1) establishing a surface temperature field, so as to allow deposition only at certain high-temperature areas, (2) controlling the distribution of vapor impinging upon the area of build up, (3) combinations of (1) and (2), and (4) through inducing dislocations or surface irregularities. Accurate control of the surface temperature distribution of an arbitrary configuration is required for the first scheme. Hence, control over thermal conductivity must be exercised. The second suggests a technique not unlike that of hot spraying. (3) Here, however, the spraying apparatus need not also be the heat source. In addition, the necessary temperatures will be much lower than those currently used in hot spraying techniques. The last scheme takes advantage of the fact that vapor deposition does not occur uniformly over a given surface, but rather preferentially at sites which are essentially geometrical irregularities.

C-1 Temperature Distribution as a Shape-Controlling Mechanism

In this process deposition takes place after a chemical reaction has released the material to be deposited. For example, tungsten hexachloride is reduced by hydrogen gas yielding tungsten which is in the gaseous state and therefore ready for deposition. There are a number of governing factors to consider, such as temperature control and temperature distribution control.

If one uses d-c joule heating to produce the temperatures necessary to initiate the chemical reaction which will release the desired constituents at the point of deposition, it is quite obvious that the method must be restricted to small-cross-section cylindrical configurations.

Most current vapor growth experiments simply utilize a hot wire of small diameter as a deposition surface. In the initial stages of the experiment, only moderate electrical currents are needed to maintain the necessarily high deposition temperatures. As the diameter of the wire grows, the process becomes somewhat uneconomical and eventually completely impractical. Indeed, d-c joule heating of large volumes of material in order to produce a high surface temperature is not economical.

Nevertheless, for small-cross-section geometries having cylindrical symmetry, it is possible to maintain temperature gradients along the axis of symmetry by reasonably straightforward methods. For example, if one were interested in producing a thin cylinder of varying cross section, a series of induction heaters might be used to regulate the temperature along the length of the cylinder. In the simplest case, a single coil encircles the cylindrical mandrel and is moved axially in programmed fashion. Deposition then takes place at the high temperature areas adjacent to the coil only. The conduction problem can be minimized by encouraging inward radial heat flow through the use of a coolant tube inside the mandrel.

The geometry of a configuration can also be used to establish a temperature distribution through the heat flow process. For example, cone shapes can be generated by simply heating one end of a mandrel and letting axial heat flow establish a linear temperature gradient. As the cone grows, the heat source temperature (say an induction heater) would have to be regulated to maintain a linear growth gradient.

The volume heating methods described are applicable to small bodies, say, inches in size. Larger volume configurations are more economically heated by surface heating methods. The most obvious method is to turn to high-frequency a-c to utilize the skin effect in metals. Uniform cylinders can be generated in this manner.

Preferential deposition may be accomplished with an a-c surface heater source by varying either the surface impedance of the growing structure through an external surface magnetic field or by varying its total resistance. For example, a cylinder of varying cross section may be produced in the following manner in a vacuum chamber: A tube through the cylindrical mandrel carries a suitable coolant, liquid nitrogen, for instance. Vapor introduced into the chamber immediately condenses on the cold surface. A magnetic field, perpendicular to the axis of the mandrel, varies in intensity from, say, 10 to about 40 kilogauss along the axis. Under the influence of a 40-kilogauss field the surface resistance is over 100 times as large as it is near the 10-kilogauss field. Such values are typical of tungsten. Then a-c current is pulsed through the cylinder for a short period so as to raise the high-resistance areas above the threshold temperature at which the reaction takes place, while at the low-resistance areas the temperature is too low to initiate the reaction. For a 10-cm-long tungsten cylinder with a skin depth of about 10 microns, this process will use about 200 joules which boils off about 2 grams of liquid nitrogen. When the mandrel surface reaches liquid nitrogen temperature again, the cycle is repeated. The thermal strain involved would not pose a serious problem since only a very thin layer of surface material is being raised to a high temperature.

In varying the surface impedance or skin depth, the effect of a magnetic field parallel to the work surface can also be used. For example, in the case of tungsten at liquid nitrogen temperature, a field change of about 10 kilogauss could change the penetration depth by a factor of 10.

If a collimated optical beam rather than an r-f source is used for heating, the magneto-reflection effect may be used to make the penetration depth small. Hence, only very thin surface volumes are heated above the reaction threshold temperatures (with a weak unfocused laser or focused incoherent source) and the power requirement is minimized. Preferential deposition would be attained with this method by sweeping the light across particular areas.

C-2 Vapor Impingement Control

The amount of vapor reaching a certain area on a growing structure
may also be used to control growth.

In the simplest case a mandrel is heated to a level above the threshold
temperature for a given reaction and deposition is accomplished by a guided
vapor beam. In the case of tungsten deposition for example, a mixture of
tungsten hexachloride and hydrogen gas is used. The entire operation must
take place under vacuum; the residual gases may be drawn off and recycled.

The spraying procedure may be made automatic by using either elec-
trically controlled guiding or a large number of jets, each spraying a regulated
amount of vapor. The ultimate limitation in size of structure that the method
could produce would not be due to rate-of-vapor-flow limitations but, rather,
to the difficulties in maintaining the structure at the necessarily high tem-
perature. However, faced with production of a substance that is not workable
by usual methods, the power expenditures might be justified. Indeed, one
might speculate on the feasibility of diamond die production by a vapor deposi-
tion process. It might prove possible to find a reaction which would liberate
carbon atoms at a hot diamond seed surface so that incorporation into the
diamond structure would be more favorably than formation of the graphite
structure. Attempts to produce the diamond structure by vapor deposition
have not been reported, most methods centering about high pressure
techniques (32).

C-3 Combined Techniques

The most sophisticated and economical method of shape production
would consist of a combination of spraying and temperature control techniques.
For instance, a small portion of the surface of a mandrel or structure could
be raised to an elevated temperature by the light-beam technique mentioned
in Section C-1. Simultaneously, a small spray would be directed at the spot,
and decomposition and subsequent deposition would take place. The pulsed light
beam and spray would traverse the surface in phase with one another, resulting
in controlled deposition. Power expenditures would be minimized by making the
electromagnetic penetration depth small and supplying just enough energy to

heat the small area above the reaction threshold temperature. When the reaction would take place with subsequent deposition occurring, the small amount of residual thermal energy would be conducted into the lattice, causing a barely perceptible rise in over-all temperature. The electromagnetic energy supplied in any such process will be large. Since this energy is generated in small increments, it may be possible to conduct the energy away from the surface and hence insure that the surface temperature is below threshold at all places except the deposition site. For example, to increase the radius of a 10-cm-long tungsten cylinder from 1 to 2 cm, it is necessary to supply a total of about 10^5 joules to attain a 1000°C theshold temperature - the energy consumed in 1.5 hours by a 150-watt incandescent lamp. Since the average power is low, maintaining a low background temperature by means of conduction would present no unusual problem.

To appreciate the economy of this differential deposition procedure, consider the amount of total energy required to maintain the entire volume of the tungsten rod at a threshold temperature of about 1000°C! If one assumes that the deposition can take place in 10 hours - a short time for vapor deposition processes - approximately 10^8 joules must be supplied. For large surface areas, the power requirements to maintain a 1000°C temperature would be impractically great.

C-4   Vapor Phase Growth Control Through Induced Dislocations or Surface Irregularities

The surface irregularities of a substance are instrumental in determining growth rate during vapor deposition. Therefore, shape control by means of this mechanism is suggested. The procedure involves inducing a large number of surface irregularities at chosen areas during deposition. The actual creation of the necessary absorption sites or surface irregularities may be carried out by a number of methods.

C-4.1   Hot or Cold "Probing"

During the deposition process the growing material is "jabbed" or "probed" with a needle at chosen areas. Arrangements are made to maintain the needle at a temperature suitable for the production of disturbances

in the lattice and the successful withdrawal of the needle, intact. Preferential deposition will take place at these "sore spots" and growth control is achieved thereby. Conceivably, both micro- and macro-probing techniques can be developed, the former utilizing specially grown whiskers and the latter super-alloy needles. A "sewing machine" type device can be guided over the growing surface and its path automatically controlled. The time of traverse of the machine across the surface must be such as to allow sufficient out-growth of "sore" spots before fresh probing once again initiates growth.

Actually, growth will proceed to some extent over the entire surface subjected to a vapor, even if the pressure is low enough to suppress spontaneous nucleation. Therefore, success of the probing method will depend somewhat on finding appropriate operating conditions.

C-4.2   Electric Field Probing

In a manner similar to the needle technique, surface disturbances can be produced by raising an external probe to high potential and bringing it close enough to the growing material to cause a small discharge or breakdown current to flow between probe and surface. This current will cause severe local heating and structure deformation, hence encouraging deposition.

Alternatively, one could operate with a probe potential below the breakdown value of the current. Large local surface-charge density and strong polarization of adjacent vapor atoms would result. Although the effect of this polarization on the deposition mechanism has not been investigated in detail, some preference for deposition at these sites would be established.

C-4.3   Particle Bombardment

Perhaps the most obvious method of producing localized surface damage or disturbance is by bombarding the growing material during deposition either on the microscopic or macroscopic scale.

In particular, small seeds (as large as sand grains) may be impinged on a growing structure with a velocity just sufficient to embed them

in the surface. These seeds then act as growth nuclei. The rate at which they are thrown at the surface will depend on the vapor pressure and subsequent deposition rate. In addition, they must be of a size small enough to come to thermal equilibrium with the growing structure in a short period of time and be readily bonded into the lattice.

On the microscopic scale, consider the use of atomic ions in forming surface nucleation sites during deposition. A beam of very low current density having energy sufficient to produce localized surface damage is controlled by the usual electric or magnetic means. The beam is simultaneously pulsed and swept across the deposition surface. Preferentially, ions of the same species as the deposition material are used in order to optimize momentum transfer at the surface and prevent deep penetration.

In conclusion, further investigation of the foregoing shape control schemes is planned.

APPENDIX D

ELECTRICAL EFFECTS IN IONIC CRYSTALS

References to the interaction of electric and stress fields in ionic crystals were briefly discussed in the Second and Third Interim Report (1,11). Recognition of the relevance to producibility of direct action of electric fields on a material led to the fundamental discussion below.

In the broad area of materials and producibility, a knowledge of the characteristics of ionic crystals is of dual importance. From a research point of view, the ionic bond is rather better understood than the metallic bond; in addition, some experimental techniques feasible with ionic crystals are either difficult or impossible with metal crystals. Among these are etch-pitting procedures for the detection of dislocations and the use of polarized light microscopy for investigations of strain fields. Thus, quantitative experiments are easier to design and carry out with ionic crystals.

From a more practical viewpoint, ionic binding is the dominant mechanism of inter-atomic binding in ceramic materials for high temperature application. Currently these materials represent a largely untapped source of structural materials for aerospace applications, although the problem of insufficient ductility remains to be solved.

In this appendix some important aspects of ionic crystal behavior are described. Since many characteristics of ionic crystals are explicable in terms of defects or imperfections in the crystal structure, the discussion is organized in terms of type of defect.

D-1 Point Defects in Ionic Crystals

The simplest defect in any crystal structure is the point defect or vacancy, for it consists simply of a site in the crystal lattice which is not occupied by the expected atom or crystal lattice which is not occupied by the expected atom or ion. In a model which regards the crystal as an assembly of hard spheres rigidly fixed at the points of a space lattice, the vacancy is just a missing hard sphere. However, in a real crystal there will be some

relaxation around the vacant site, i.e., the neighboring atoms or ions will be slightly displaced from their usual spatial positions, and the frequency of their thermally induced vibrations will differ from the usual frequency. Further, the vacancy is a thermodynamically stable entity, in contrast to dislocations or line imperfections, which are thermodynamically unstable.

D-1.1 Geometry

There are two essentially different types of point imperfections in ionic crystals, the Schottky defect and the Frenkel defect (32, 33, 34). They are indicated in Figure D-1.

The Schottky defect may be described conceptually as the transfer of an ion from the interior of the crystal to its surface. To accomplish this transfer, a characteristic amount of energy must be supplied, which is frequency of the order of one to two electron volts. Some of this energy is recovered by lattice relaxation around the defect thus formed.

A most important aspect of defect formation is the electric polarization of the lattice in the vicinity of the defect. A unit negative
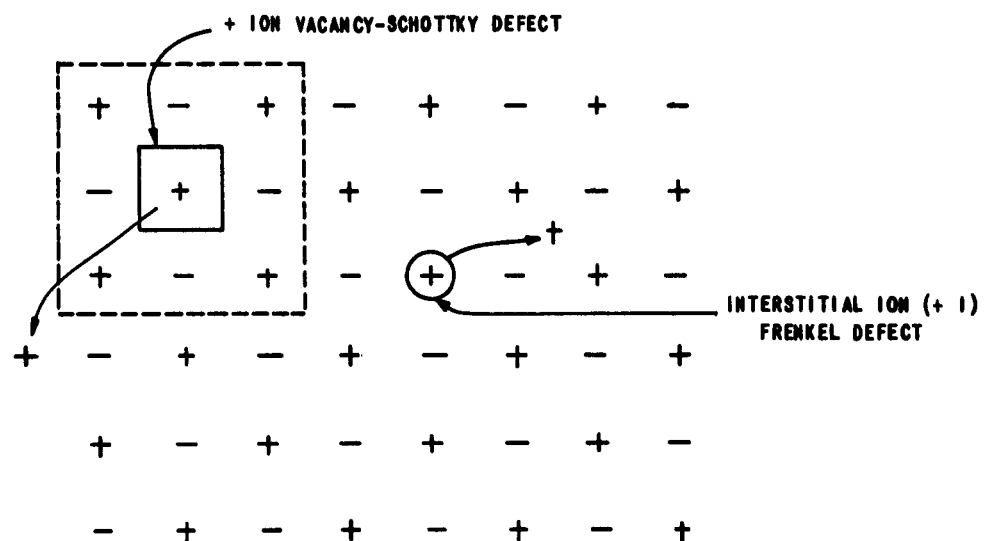
Figure D-1   THE FRENKEL AND THE SCHOTTKY DEFECT

charge is associated with a <u>positive</u> ion vacancy. Considering the cell outlined by the dotted lines, there are four positive corner ions which contribute one-fourth of a positive charge each to the dotted cell, and there are four negative side-centered ions which contribute one-half of a negative charge each to the dotted cell. Therefore, there is a net negative charge resulting from the positive ion vacancy. From identical reasoning there is a net positive charge associated with each negative ion vacancy. In first treatments (33,34,35) of the properties of ionic crystals, it is postulated that the crystal must remain electrically neutral. This condition can be met only if positive and negative ion vacancies occur in equal number; in this case, it is customary to speak of the energy of formation (E_p) of a vacancy pair, where one of the pair is a positive ion vacancy and the other is a negative ion vacancy. However, this does not imply that the energies of formation of positive and negative ion vacancies are equal.

Diffusion and electrical conductivity are closely related in ionic crystals (36). The atomic mechanism of diffusion or mass transport is interchange between vacancies and their neighbors; for evident electrostatic reasons a positive ion vacancy will exchange positions with one of the neighboring positive ions, and a negative ion vacancy with one of its neighboring negative ions. Since the vacancy is an electrically charged entity this is equivalent to a transport of charge, and the atomic mechanisms of mass transport and charge transport are identical. For this reason measurements of electrical conductivity are one of the most powerful methods for studying the production and mobility of point defects in ionic crystals. This technique is not feasible with metal crystals.

The Frenkel defect may be described as the removal of an ion from a normal lattice site and subsequent insertion of the ion into an interstitial position (Figure D-1). Once again a characteristic energy of formation is involved, and once again removal of the ion results in the vacancy having a charge opposite in sign to that of the ion. However, with the Frenkel defect the interstitial introduces a local charge of the same sign as the interstitial. The Frenkel defect, vacancy plus interstitial, is thus electrically neutral, and there is no necessity for equal numbers of positive and negative ion Frenkel defects.

There are geometric restrictions on the formation of Frenkel defects. The crystal structure must contain an interstitial site of sufficient size to accommodate the ion. For this reason Frenkel defects are most often found in the silver halides, and Schottky defects are found in the alkali halides.

D-1.2 Association of Defects

In the preceding discussion each defect has by implication been considered as a separate entity, isolated from the influence of any other defect. For example, in the discussion of the pair of vacancies which constitute a neutral Schottky defect, a possible interaction between the positive and negative ion vacancies was not considered. In fact, since these two vacancies are oppositely charged, an electrostatic interaction of attraction must exist, and this has been observed. Therefore, a significant fraction of the Schottky vacancies may exist as near neighbor pairs with a definite interaction energy.

Another and important defect association arises from the presence of ionic impurities having a valence different from the corresponding ion of the pure crystal. The commonest example is a positive divalent impurity ion, say Ba or Ca, in a crystal with univalent positive ions, say KCl or NaCl. Since the impurity ion is divalent, there is a net unit positive charge in its vicinity. To maintain electrical neutrality a negative charge must be present to neutralize the net positive charge of the impurity; the evident source of this negative charge is a positive ion vacancy. Therefore, positive ion vacancies will associate with impurity ions, and in such crystals the vacancy concentration is determined by the impurity concentration. Supporting evidence for this picture is presented in Figure D-2.

Since the impurity ion-vacancy pair is electrically neutral, diffusion of the pair does not contribute to the electrical conductivity. This is also true of associated Schottky vacancies. A summary picture of point defect geometries is presented in Figure D-3.
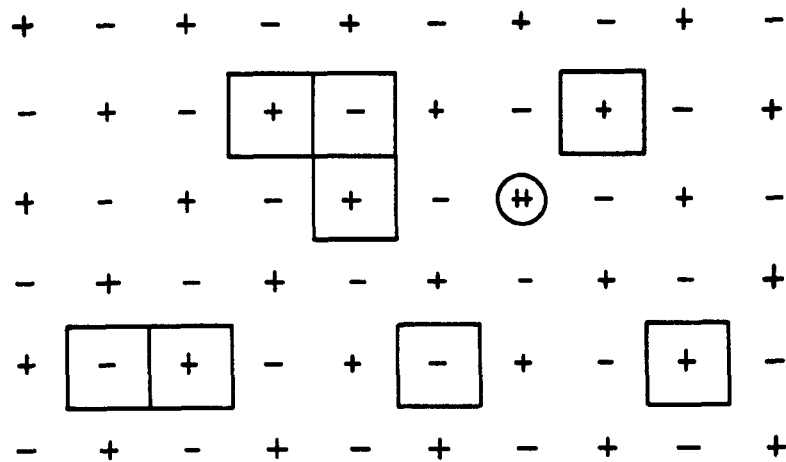
D-1.3 Concentration of Point Defects

Point defects are equilibrium constituents of a crystal, as can be shown by a thermodynamic calculation which also gives the equilibrium

① Best fit for experimental results

② Change in density expected if the densities of the two salts were purely additive

③ Change in density expected if the Ca^{++} ion plus vacancy occupied the same volume as two K^{+} ions
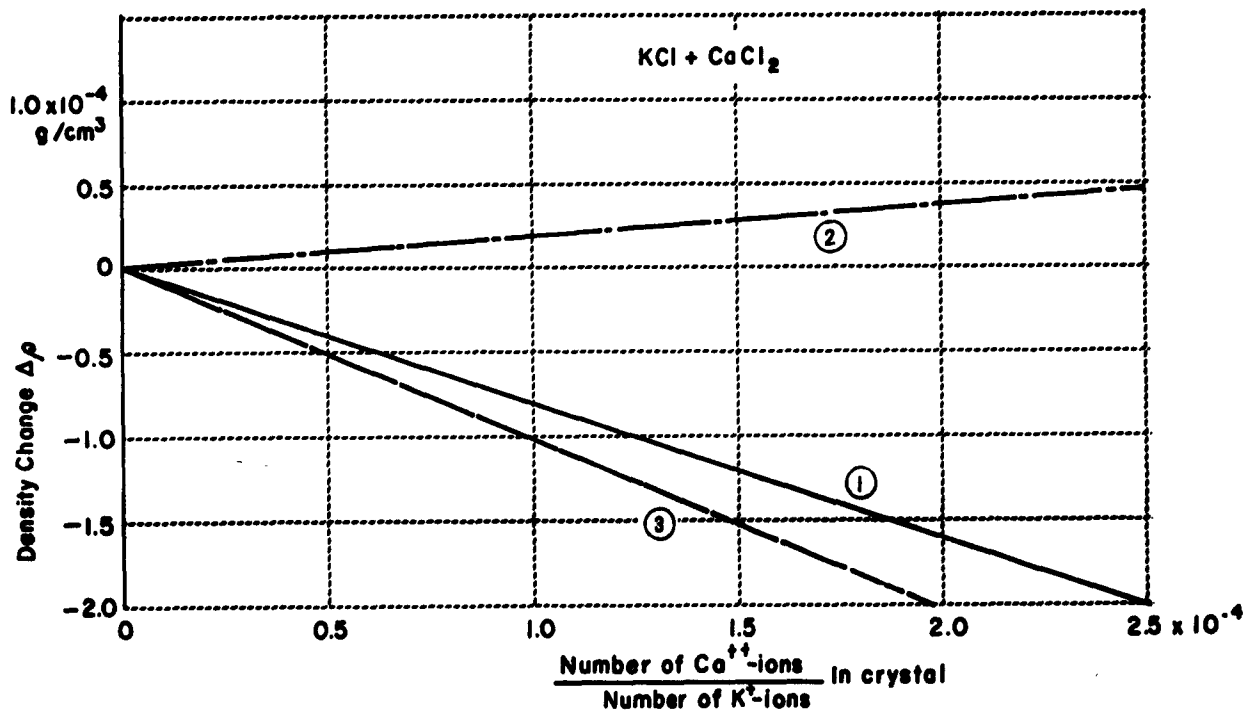
From Reference (33)

Figure D-2 THE CHANGE IN DENSITY AS A FUNCTION OF
DIVALENT ADDITION FOR KCl CONTAINING CONTROLLED
AMOUNTS OF $CaCl_2$

+   −   +   −   +   −   +   −   +   −

−   +   −   [+   −]   +   −   [+]   −   +

+   −   +   −   [+]   −   (+)   −   +   −

−   +   −   +   −   +   −   +   −   +

+   [−   +]   −   +   [−]   +   −   [+]   −

−   +   −   +   −   +   −   +   −   +

From Reference (33)

AS DISPLAYED FROM UPPER LEFT TO LOWER RIGHT AND READING
ACROSS, THE UNITS ARE: POSITIVE-ION VACANCY; NEGATIVE-ION
VACANCY; COUPLED PAIR OF VACANCIES OF OPPOSITE SIGN;
DIVALENT ION PRESENT SUBSTITUTIONALLY WITH ASSOCIATED
POSITIVE-ION VACANCY; CLUSTER OF TWO POSITIVE-ION
VACANCIES AND ONE NEGATIVE-ION VACANCY.

Figure D-3 POINT DEFECT GEOMETRIES

concentration of defects as a function of energy of formation and temperature (33, 34, 35, 36). Thus an ideal crystal, ideal in the sense that all lattice sites are occupied by host atoms and no impurities or vacancies are present, is a thermodynamic impossibility. A general discussion of this calculation is given by Frenkel in Kinetic Theory of Liquids (34); an outline of the approach and results for special cases are considered here.

Consider an ionic crystal of two oppositely and singly charged ion species, with no impurities and only simple point defects. These defects are labeled according to the following scheme.

Defect	Symbol	Associated Charge
Positive ion vacancy	$N_A{}'$	-
Positive ion interstitial	$N_A{}''$	+
Negative ion vacancy	$N_B{}'$	+
Negative ion interstitial	$N_B{}''$	-

The condition of macroscopic electric neutrality of the crystal requires that

$$N_A{}' + N_B{}'' = N_A{}'' + N_B{}'$$

(1)

where the N's now refer to the total number of defects of the indicated type in the crystal. The change in free energy of the ideal crystal when the indicated defects are introduced is given by

$$\Delta G = G_A{}' + G_B{}' + G_A{}'' + G_B{}''$$

(2)

where, for example, $G_A{}'$ is the free energy change resulting from the introduction of $N_A{}'$ positive ion vacancies, and the other G terms are similarly defined. Each G term is represented by an equation of the form, for example,

$$G_A{}' = N_A{}' E_A{}' - kT \left\{ I_n\, N_A{}! - I_n\, N_A{}'{}! - I_n\, (N_A - N_A{}')! \right\}$$

(3)

where

k = Boltzmann's constant

$E_A{}'$ = Energy to form one positive ion vacancy

N_A = Total number of sites which are available to positive ion vacancies

T = Temperature in °K

Similar equations exist for $G_A{}''$, $G_B{}'$, and $G_B{}''$. They are developed from the general thermodynamic relation

$$G = H - TS \tag{4}$$

Where in this case $H = N_A{}' E_A{}'$ and S is approximated solely as the change in configurational entropy S_c resulting from the introduction of $N_A{}'$ positive ion vacancies. The configurational entropy is computed from the Boltzmann equation

$$S_c = k \ln W \tag{5}$$

where W is the number of distinguishable configurations of $N_A{}'$ positive ion vacancies among $N_A{}'$ possible sites. This development assumes the vacancy concentration to be sufficiently small that no two vacancies are close enough to interact. Thus, an equation such as (3) exists for each type of point defect in the crystal.

It is customary to replace the factorial terms in (3) with the use of Stirling's approximation for large X

$$\ln X! = X \ln X - X \tag{6}$$

Equation (3) then becomes

$$G_A{}' = N_A{}' E_A{}' - kT \left\{ N_A \ln N_A - (N_A - N_A{}') \ln (N_A - N_A{}') - N_A{}' \ln N_A{}' \right\} \tag{7}$$

Similar equations exist for G_A'', G_B', and G_B''; their sum constitutes the change in total free energy accompanying the introduction of the indicated number of each type of defect into the crystal.

It is now possible to outline the procedure whereby the equilibrium number of defects is calculated as a function of the energy of formation and the temperature. The technique is that of undetermined multipliers, i.e. equation (3) is differentiated with respect to N_A', N_A'', N_B', N_B'' separately, and in each differentiation the macroscopic neutrality condition, equation (1), is used as the restraining condition. This amounts to minimizing ΔG with respect to concentration under the condition that electrical neutrality is not violated. The following four equations result

$$N_A' = N e^{+\left(\frac{\mu - E_A'}{kT}\right)} \qquad N_A'' = N e^{-\left(\frac{\mu + E_A''}{kT}\right)}$$

$$N_B' = N e^{-\left(\frac{\mu + E_B'}{kT}\right)} \qquad N_B'' = N e^{+\left(\frac{\mu - E_B''}{kT}\right)}$$

(8)

where μ = undetermined (Lagrangian) multiplier,

$$N_A = N_B = N$$

The Lagrangian multiplier is evaluated by substituting equations (8) into (1) to yield

$$\mu = \frac{kT}{2} \ln \left\{ \frac{e^{-E_A''/kT} + e^{-E_B'/kT}}{e^{-E_A'/kT} + e^{-E_B''/kT}} \right\}$$

(9)

which in turn enables one to write

$$N_A' N_A'' = N^2 e^{-\left(\frac{E_A' + E_A''}{kT}\right)}$$

$$N_B' N_B'' = N^2 e^{-\left(\frac{E_B' + E_B''}{kT}\right)}$$

(10)

These are the most general equations for the equilibrium concentration of unassociated positive and negative ion vacancies and interstitials as a function of temperature. The major assumptions are

1. The energies of formation are independent of temperature,

2. The concentrations are sufficiently small that individual point defects do not interact,

3. The entropy change associated with point defect introduction is assumed to be entirely configurational entropy, i.e., relaxation of the ions around the point defect is ignored. Numerous calculations of this effect suggest that it does not change the results by a factor of more than two.

The general equations (10) may be readily specialized to the Schottky and Frenkel defects discussed previously.

In the case of Schottky defects, only positive and negative ion vacancies are considered, and equations (10) become

$$N_A' = N e^{-E_A'/kT}$$
$$N_B' = N_e^{-E_B'/kT}$$

(11)

If the electrical neutrality condition is applied, then $N_A' = N_B'$, and there is no way of experimentally separating E_A' from E_B'. Consequently, it is customary to write

$$E_A' = E_B' = \frac{1}{2} E_p$$

(12)

where E_p is the energy of formation of an unassociated Schottky pair. Then equations (11) may be written as

$$N_p = N e^{-E_p/2kT}$$

(13)

where N_p is the number of Schottky pairs. The concentration of Schottky pairs thus increases exponentially with temperature; the insertion of typical values of E_p indicates an approximate concentration at 1000°K of 10^{-5}.

In a similar fashion the number of Frenkel defects (vacancy plus unassociated interstitial) is given as a function of temperature by

$$N_p = (N_1 N_2)^{1/2} e^{-E_p/2kT}$$

(14)

where

N_p = Number of Frenkel pairs

E_p = Energy to form Frenkel pair

N_1 = Number of lattice sites for vacancy

N_2 = Number of lattice sites for interstitials

Once again an exponential dependence of concentration upon temperature is obtained.

D-1.4 Divacancies and Higher Order Complexes

In the previous discussion of Schottky and Frenkel defect concentrations, each individual point defect has been treated as though isolated from all others. The method of calculation may also be extended to associated vacancies, and the case of associated Schottky defects, i.e., pairs of adjacent positive and negative ion vacancies, is considered here. The crystal is considered to contain N_D divacancies scattered amongst N lattice sites, with $N_D \ll N$. The number of distinguishable arrangements W may be calculated as indicated in the following table. The energy of formation of the divacancy is E_D, and Z is the coordination number (number of near neighbor sites) of the particular crystal structure.

N_D	No. of ways 1st vacancy may be added	No. of ways 2nd vacancy may be added
1	$N - 2N/2$	Z
2	$N - 2 = 2(N/2 - 1)$	Z
3	$N - 4 = 2(N/2 - 2)$	Z
.	"	"
.	"	"
.	"	"
.	"	"
.	"	"
N_D	$(N - 2N_D + 2) = 2(N/2 - N_D + 1)$	Z

The total number of arrangements of N_D divacancies among the N lattice sites is then

$$z^{N_D} 2^{N_D} \left\{ (N/2)(N/2 - 1)(N/2 - 2) \cdots (N/2 - N_D + 1) \right\}$$

To obtain the number of distinguishable arrangements, the above must be divided by the number of indistinguishable arrangements, which is the product of $N_D!$ and 2^{N_D}. Therefore W, the number of distinguishable arrangements, is given by

$$W = \frac{z^{N_D}(N/2)!}{N_D!\,(N/2 - N_D)!} \tag{15}$$

and the corresponding equation for the free energy change upon adding N_D divacancies is

$$\Delta G = N_D E_D - kT \ln \frac{z^{N_D}(N/2)!}{N_D!\,(N/2 - N_D)!} \tag{16}$$

When ΔG is minimized with respect to N_D, the resulting equation for the concentration of divacancies as a function of temperature is

$$N_D = N \frac{z}{2} e^{-E_D/kT}$$

(17)

where $Z/2$ is an orientation factor which gives the number of possible spatial orientations of the divacancy. For a point defect complex composed of r point defects, the concentration would be given by

$$N_r = N P_r e^{-E_r/kT}$$

(18)

where P_r is the number of distinguishable orientations that the r-order complex can assume.

D-1.5   Equilibria Among Point Defects

More than one type of point defect may exist in a crystal, and it then becomes of interest to consider the interaction among them. The law of mass action is used to express the equilibrium concentrations. One example will be discussed, the reaction between divacancies and single vacancies, which may be expressed as

$$\text{Two vacancies} \rightleftharpoons \text{one divacancy}$$
$$2v \rightleftharpoons d$$
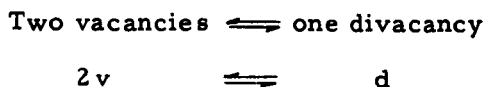
The "equilibrium constant" K for this reaction is

$$K = c_d / c_v^2$$

(19)

the concentration of the divacancies divided by the square of the concentration of the vacancies. K is, in turn, related to the energy change accompanying the reaction, $E_D - 2E_v$ by

$$K = e^{-(E_D - 2E_v)/kT}$$

(20)

NM-1559-P-4

E_D = Energy of formation of divacancy

E_v = Energy of formation of single vacancy

Therefore, the single and divacancy concentrations are related by

$$C_d = c_v^2 e^{-(E_D - 2E_v)/kT}$$

(21)

Since the net value of the exponential is usually positive, the concentration of divacancies relative to single vacancies is more important at low temperatures. Other point defect equilibria problems may be handled in the same fashion.

D-1.6   Conductivity and Diffusion

Since single vacancies in ionic crystals are electrically charged, their motion constitutes both diffusion and conduction of current. The inter-relation of these phenomena will be described briefly (36). The development is in terms of the drift of charged point defects under the influence of a uniform electric field Figure D-4. The probability per unit time that a positively charged entity will move with the field is

$$\nu e^{-(E_M - \frac{1}{2} eaF)/kT}$$

and against the field

$$\nu e^{-(E_M + \frac{1}{2} eaF)/kT}$$

The mean drift velocity v will be the difference of these quantities multiplied by the jump distance a.

$$V = a\nu \left(e^{-(E_M - \frac{1}{2} eaF)/kT} - e^{-(E_M + \frac{1}{2} eaF)/kT} \right)$$

(22)

$$= 2a\nu e^{-E_M/kT} \sinh \left(\frac{1}{2} eaF/kT \right)$$

(23)

APPLIED FIELD F
$$F = -\partial\phi/\partial x$$
$$\therefore \phi = Fa$$
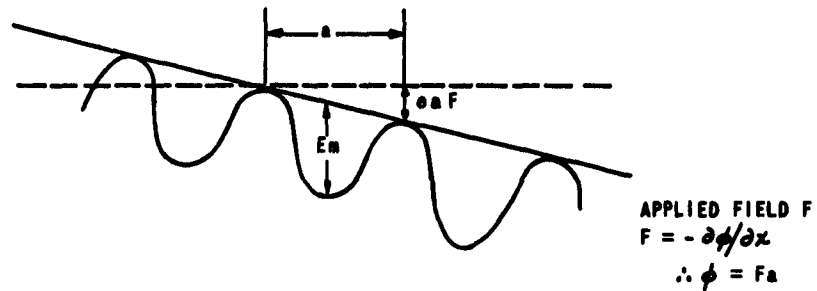
APPLIED FIELD CAUSES CHANGE IN ACTIVATION
ENERGY FOR MOVEMENT FROM ONE SITE TO ANOTHER
BY

+ 1/2 eaF   IF ION MOVES AGAINST FIELD

- 1/2 eaF   IF ION MOVES WITH FIELD

**Figure D-4   DRIFT OF CHARGED POINT DEFECTS UNDER THE
INFLUENCE OF A UNIFORM ELECTRIC FIELD**

Since eaF << kT,   the hyperbolic sine may be expanded in a series and the
first term taken.

$$V = a\nu e^{-\varepsilon_m/kT} \frac{eaF}{kT}$$

(24)

The ionic mobility u is defined as the relation between the drift velocity v
and the electric field F, i.e.,

$$u = \frac{\nu e a^2}{kT} e^{-\varepsilon_M/kT}$$

(25)

The electric conductivity arising from a single defect type is

$$\sigma = \text{(no. of defects) (mobility of defect) (charge on defect)}$$

or

$$\sigma = \frac{N e^2 \nu a}{kT} e^{-(\varepsilon_F/2 + \varepsilon_M)/kT}$$

(26)

where the number of defects is taken from the formula for the concentration of Schottky defects developed earlier. Thus, the intrinsic ionic conductivity is exponentially dependent upon temperature.

The relation between conductivity and diffusion is not easily established, for the diffusion coefficient is given by

$$D = \nu a^2 e^{-\left(\frac{E_P}{2} + E_M\right)/kT}$$

(27)

therefore,

$$\frac{\sigma}{D} = \frac{N e^2}{kT}$$

(28)

under the assumption that both diffusion and current flow result from movement of a single point defect type. Thus, equations (26) through (28) describe intrinsic conductivity and diffusivity.

Substantial experimental evidence has been adduced to show that the previous picture is correct in the high temperature or "intrinsic" range. For good quality alkali halide crystals this temperature range is in excess of 550°C. At these temperatures the dominant defect type is Schottky vacancy pairs generated by the requirements of thermal equilibrium.

Substantial deviations from the simple picture presented above occur at lower temperatures; it is found that the electrical conductivity is substantially higher than predicted by equation (26). This suggests that the Schottky vacancy pairs, whose concentration is greatly diminished at lower temperatures, are no longer controlling the conductivity.

Divalent impurity ions are thought to be responsible for this effect; in investigations of alkali halide crystals of controlled impurity content, it has been shown that the increase of the conductivity above the intrinsic value is proportional to the impurity concentration. Typical results for KCl containing different concentrations of $SrCl_2$ are reproduced in Figure D-5.

To preserve macroscopic electric neutrality, a given concentration of divalent impurities in a monovalent crystal must be accompanied by
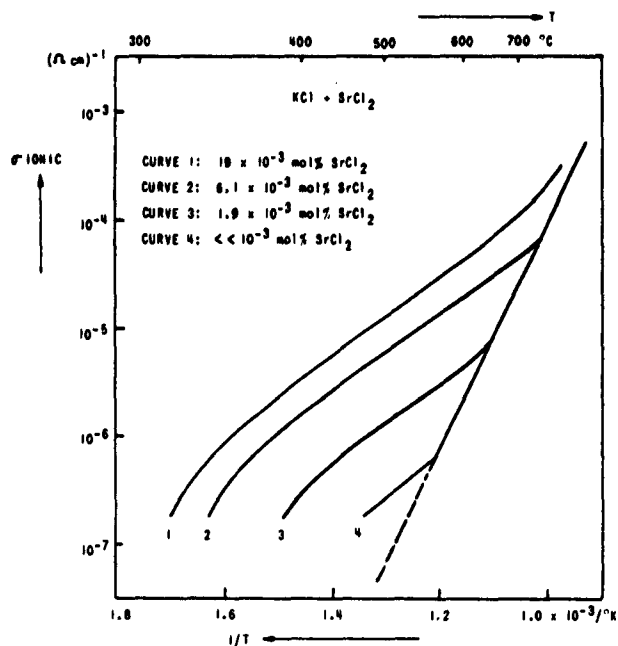
Figure D-5 INCREASE IN CONDUCTIVITY OF KCl BY SMALL AMOUNTS OF SrCl$_2$

From Reference (35)

an equal concentration of positive ion vacancies. Thus, at low temperatures the concentration of positive ion vacancies required by the divalent impurities is far greater than the thermally generated vacancy concentration, and the conductivity is controlled by the impurity concentration (35). The divalent impurities and positive vacancies are considered to be almost wholly unassociated, and the positive ion vacancies are thus considered free to contribute to the electrical conductivity. The degree of association will increase, however, as the temperature is lowered. The different slopes of the conductivity curves in the high and low temperature regions results because the low temperature conductivity is controlled primarily by the activation energy for migration, whereas high temperature conductivity involves energies of both formation and migration.

D-1.7 Distribution of Defects in Annealled Crystals: Space Charge

To this point it has been assumed that in a pure crystal the number of positive-ion and negative-ion vacancies is identical in order to preserve macroscopic electrical neutrality. On the other hand, theoretical calculations (36) suggest strongly that the energies of formation of positive and negative-ion vacancies are not equal. Thus, it would be expected that the positive ion vacancy would be present in the greatest quantity since it would have the smallest formation energy. Then the crystal would no longer be electrically neutral in a macroscopic sense (34, 35, 37).

The situation is most easily described by considering the formation of vacancies at the surface of a pure crystal heated to an elevated temperature. Since positive ion vacancies have a lesser energy of formation, they will form in greater quantity, and the crystal must of necessity display an internal space charge Q given by

$$Q = e \left(N_B - N_A \right)$$
(29)

where e is the electronic charge, and N_A and N_B are the numbers of positive and negative-ion vacancies, respectively. Since the formation of a vacancy at a surface leaves an excess ion upon the surface, Figure D-5, the internal space charge will be balanced by a surface charge of opposite sign, -Q. This separation of charges must be accompanies by an electric field which tends to restore the neutral condition. Designating the potential of this field by ϕ, and repeating the derivation given earlier, the number of positive- and negative-ion vacancies per unit volume will be given by

$$n_A = n \, e^{-(E_A - e\phi)/kT}$$
(30)

$$n_B = n \, e^{-(E_B + e\phi)/kT}$$
(31)

where E_A and E_B are the energies of formation of positive- and negative-ion vacancies, respectively. The potential ϕ is given as a function of the spatial coordinates by

$$\nabla^2 \phi = 4\pi \rho / \varepsilon \tag{32}$$

where ε is the dielectric constant and ρ is the net electric charge per unit volume. With the substitution

$$\psi = \frac{e\phi}{kT} - \frac{(E_A - E_B)}{2kT} \tag{33}$$

Poisson's equation becomes

$$\nabla^2 \psi = k^2 \sinh \psi \tag{34}$$

with

$$k^2 = \frac{8\pi e^2 n}{\varepsilon kT} e^{-(E_A + E_B)/2kT} \tag{35}$$

It should be noted that equation (34) is identical to the Debye-Huckel equation for the potential distribution in an electrolyte solution around an electrode. For the case of space charge in a crystal, equal concentrations of positive-ion vacancies and negative-ion vacancies will occur at positions remote from the crystal surface; the concentration of vacancies of both signs is given by $n e^{-(E_A + E_B)/2kT}$.
The quantity $1/K$ is a measure of the depth of the surface layer where the concentrations of the two vacancy types are different. Thus, the body of the crystal is electrically neutral and a space charge layer exists at the surface and extends to a depth $1/K$. The potential between surface and body of the crystal is

$$\phi = \frac{(E_A - E_B)}{2e} \tag{36}$$

From equation (35), the depth of the space charge layer is expected to decrease with temperature; rough calculations indicate that for NaCl the depth might change from approximately 2.2×10^{-5} cm at $600°$K to 1.3×10^{-6} cm at $900°$K.

Perhaps a word of caution is advisable at this point. The existence of the space charge layer has not been experimentally proven. Thus, if vacancies can be formed only in neutral pairs, or if the theoretical calculations are inaccurate and E_A approximates E_B, then a space charge layer will not exist. If the effect is real, however, it will be important, for a space charge layer should also exist around dislocations, as will be discussed in the next section. Further, the surface space charge layer would influence conductivity, diffusion, the photoelectric effect, and the photographic effect.

D-2   Line Defects in Ionic Crystals

Although it has often been suggested that the micro-plastic behavior of ionic crystals is similar to that of metals, it is nevertheless true that electrical effects may strongly influence dislocation behavior in ionic crystals, and these effects have no counterpart in metallic crystals. At present this field is in a state of considerable uncertainty; one is therefore limited to summarizing the available information with the understanding that current and future experimental work may substantially alter the picture.

D-2.1   Glide Planes and Glide Directions

From a classical, crystallographic point of view the dominant features of plastic deformation are the experimentally observed glide planes and glide directions. In metal crystals deformed under normal temperature and stress systems the operative glide systems are the crystallographic plane of greatest atomic density (and hence maximum interplanar spacing) and the crystallographic direction of greatest line atomic density. These simple generalizations of experiment are not obeyed completely by ionic crystals (38).

In crystals where the inter-atomic bond is virtually all ionic, such as NaCl, MgO, etc., deformation usually occurs by slip on $\{110\}$ planes and in $<1\bar{1}0>$ directions. The $<1\bar{1}0>$ direction is the shortest translation vector of the crystal structure, and thus the crystallographic direction of greatest atomic density; in addition, translation in a $<1\bar{1}0>$ direction does not require any near-neighbor ions of the same polarity to come into unusually close contact. Thus, no substantial electrostatic repulsive forces develop when translation occurs in this direction.

It is somewhat more difficult to account for glide on $\{110\}$ planes, for the planes in this crystallographic family are not as atomically dense as are planes in the $\{100\}$ family. It appears probable that electrostatic faulting may account for the inability of $\{100\}$ planes to function as primary glide planes (38). It has been pointed out that when a crystal has glided half a unit translation distance on a $\{100\}$ plane, the ions on the slipping planes are in an electrically neutral position. That is, each ion has equal numbers of oppositely and similarly charged neighbors at equal distances. There is then no net binding between near neighbor ions across the glide plane. To attain such a configuration a substantial amount of work is required, and under ordinary conditions, therefore, the $\{100\}$ planes do not act as glide planes.

At high temperatures the $\{100\}$ planes may become active, retaining $<110>$ as the glide direction. Even at room temperature some crystals, e.g., PbTe, will slip on $\{100\}$, while crystals such as AgCl show little preference for any glide plane, i.e., they show wavy glide. The tendency of crystals to glide on $\{100\}$ planes increases with increasing polarizability of the ions, which is equivalent to associating $\{100\}$ glide with a decrease in the ionic nature of the inter-atomic bond.

D-2.2   Dislocations in Ionic Crystals

A dislocation line is simply a line on the glide plane which separates the glided and unglided portions of the glide plane. Severe distortions in crystal structure occur only within a few atom distances of the dislocation line; this badly distorted region is called the core.

Two geometrically idealized types of dislocations are recognized, the screw and the edge dislocation. The screw dislocation may be characterized as a line around which the atom planes wind in a helical pattern. This pattern is symmetric and therefore the screw dislocation can move on any crystal plane.

On the other hand, the edge dislocation is usually described in terms of extra half planes of atoms. For ionic crystals two extra half planes, one each of positive and negative ions are necessary, in order to maintain electric neutrality. The distortion pattern around an edge dislocation is distinctly asymmetric and so a definite glide plane is associated with it. For an edge dislocation to move off of its original glide plane, the extra half plane must become either longer or shorter. This process, called climb, can only occur by absorption or expulsion of ions from the edge of the half planes, which in turn will occur only if ions can diffuse toward or away from the dislocation. In summary, climb is controlled then by diffusion, and is much more rapid at elevated temperatures.

D-2.3   Jogs in Dislocations

When the dislocation line does not lie on a single glide plane, and it rarely will, it transfers from one plane to another by offsets called jogs. Jogs are offsets in a dislocation line which do not lie in the primary glide plane. Edge dislocation jogs can be eliminated by adding or subtracting ions or vacancies at the edge of the extra half planes, while jogs in screw dislocations can be eliminated by glide along the screw dislocation line. A vacancy in the line of ions comprising the bottom of the extra half plane may be considered to be two jogs.

Jogs are of special interest in ionic crystals because they are sometimes charged. The two $(0\bar{1}1)$ extra half planes associated with an edge dislocation do not end at equal heights above the glide plane. The bottom of each extra half plane consists of a row of ions of alternate sign. With respect to jogs two possibilities may be recognized. A jog consisting of two (011) planes in height will produce a neutral jog since the alternation of plus and minus ions does not change. However, a jog consisting of one

(011) plane in height will be charged, since two ions of the same sign are next to each other. The charge is one-half the charge of one of the neighboring ions, and thus may be either positive or negative. Jogs in screw dislocations are considered not to be charged.

There are two primary sources of jogs on edge dislocations: intersection with other dislocations and equilibrium with point defects in the crystal around the dislocation. When two dislocations intersect, each becomes jogged by an amount equal to the component of the Burgers vector of the other dislocation that lies perpendicular to the glide plane of the first. With ionic crystals the geometry of the intersecting dislocations determines whether or not the jogs will be charged. If the Burgers vector of the stationary dislocation is parallel to that of the moving dislocation, no jogs will be formed upon inter-section. If the two Burgers vectors are perpendicular and that of the stationary dislocation is perpendicular to the glide plane of the moving dislocation, then a neutral jog will be formed. Charged jogs will occur only when the two Burgers vectors are oblique.

Although jogs in screw dislocations are not charged, it is true that the intersection of screw dislocations will lead to the production of charged point defects, either vacancies or interstitials, and these defects cause striking changes in physical properties such as electrical conductivity, optical absorp-tion, and so on.

D-2.4   Space Charge Around Dislocations

It is generally considered that vacancies can be formed at dislocations as well as at the surface of a crystal. From the previous discussion of surface space charge, it follows then that dislocations should be charged by having a net excess of jogs of one kind, and that the dislocation should be surrounded by a cloud of vacancies of predominantly the opposite sign (39). It would also be expected that a grain boundary or substructure boundary would be charged and surrounded by a balancing layer of charged vacancies. The regions remote from the dislocation would contain equal con-centrations of positive and negative ion vacancies. With the usual assumption that the energy of formation of the positive ion is less, the dislocation or

boundary should be positively charged and surrounded by an aggregate of vacancies with a net negative charge.

The situation just described, if it exists, would certainly influence the mechanical behavior of ionic crystals. At reasonably low temperatures, for example, the charge cloud around the dislocation would be immobile. Thus if a mechanical stress displaces the dislocation line, the electrostatic field of the vacancies will be such as to restore the dislocation line to its original position. A certain minimum mechanical stress would be necessary to separate the dislocations from their charge clouds and thus cause plastic flow. This simple mechanism could in part determine the yield strength of an ionic solid.

Mobile divalent impurities modify the discussion somewhat. At low temperatures the positive ion vacancy concentration is constant and equal to the impurity concentration; analysis shows that this causes the sign of the charge on a dislocation or surface to reverse (39). At high temperatures the original description still prevails; therefore, at one particular intermediate temperature, the isoelectric point, both dislocations and surfaces are uncharged.

If a dislocation is separated entirely from its charge cloud an electric polarization is produced proportional to the product of charge and distance moved. Ideally, the movement of charged dislocation should be accompanied by a potential between electrodes connected by a low resistance circuit. This effect would not be expected in homogeneous mechanical deformation, however, for equal numbers of dislocations are moving in opposite directions, and no net effect should result. During inhomogeneous deformation, however, a net flow of dislocations of one mechanical sign in the same direction occurs, and charge flow has indeed been observed under these conditions (40). However, charge flow has also been observed during apparently homogeneous stressing with the effect disappearing at high temperatures. This latter observation is in agreement with the thought that charge clouds can diffuse sufficiently rapidly at elevated temperatures so that they cannot be separated from dislocations. There seems to be substantial disagreement among the results of various charge flow experiments, and generalizations concerning space charge

effects on mechanical properties of ionic crystals cannot yet be made. In
view of the relevance of side effects to electrically assisted manufacturing
processes we will follow the literature on space charge effects closely.
Feasibility experiments will be performed or recommended when appropriate.

APPENDIX E

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that were the subject of earlier interim re-
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are concepts for two new process categories
that exploit phenomena better known for their
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1. Introduction
2. Guide Lines for Process
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3. Material-Removal Processes
4. Material-Addition Processes
5. Material-Displacement
   Processes
6. Program for Next Period
Appendices
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B   Cavitation
C   Shape Control in Vapor
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D   Electrical Effects in Ionic
    Crystals
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